

tween -20 and -30° during addition. The system was warmed to room temperature and volatiles were removed through the rotary evaporator. The residue was stirred with a little ether and filtered to give 3.3 g (21%) of the red, crystalline product which melted at $238-240^\circ$. Recrystallization from glyme gave material which melted at $244-245^\circ$: ir (Nujol) 3080 (w), 2950 (w), 1720 (s), 1550 (s), 1440 (m), 1250 (s), 1200 (m), 1160 (m), 1050 (m), 940 (m), 830 (m), 820 (m), 765 (m), 730 cm^{-1} (m); uv (CH_2Cl_2) λ 444 nm (ϵ 2470), 315 (11,000), 302 (10,600) and 290 (sh, 10,000).

Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_4\text{S}_4$: C, 37.48; H, 2.52; S, 40.03. Found: C, 37.28; H, 2.54; S, 39.88.

$\Delta^{2,2'}$ -Bi-1,3-dithiole-4,4'(5')-dicarboxylic Acid (13). A heterogeneous system consisting of 3.2 g (0.01 mol) of the diester, 25 ml of 1 *N* sodium hydroxide, and 100 ml of tetrahydrofuran was heated at reflux for 45 min. The mixture was then homogeneous. It was acidified with 1 *N* hydrochloric acid and filtered to give 2.6 g (89%) of the red, crystalline acid. The acid did not melt under 350° : uv (0.01 *N* NaOH) λ_{max} 407 nm (ϵ 2570), 313 (13,000), 302 (12,600), 285 (sh); ir (Nujol) 3100-2500 (w), 1660 (s), 1540 (s), 1420 (s), 1290 (s), 1195 (m), 1040 (m), 840 (m), 825 (w), 775 (w), and 730 cm^{-1} (w).

Anal. Calcd for $\text{C}_8\text{H}_4\text{O}_4\text{S}_4$: C, 32.9; H, 1.4; S, 43.9. Found: C, 33.0; H, 1.6; S, 43.7.

Tetrathiafulvalene.¹⁴ A mixture of 292 mg of the diacid and 10 ml of pyridine was sealed in a heavy-walled glass tube under vacuum after flushing with argon while freeze-thawing. The tube was heated at 240° for 1.5 hr. The tube was cooled and opened and the solvent was evaporated. The dark residue was extracted twice with 10-ml portions of acetonitrile. The extracts were evaporated and the residue was sublimed at 105° (0.1 Torr) to give 140 mg (69%) of the orange product. The sublimate melted at $114-116^\circ$.

Acknowledgment. We are indebted to Eleanor G. Applegate for expert technical assistance.

Registry No.—1, 51751-15-6; 3, 31366-25-3; 3-*d*, 51751-16-7; 7, 1008-62-4; 9, 930-35-8; 10, 7396-41-0; 11, 51751-17-8; 12, 51751-18-9; 13, 51751-19-0; dimethyl acetylenedicarboxylate, 762-42-5; ethylene trithiocarbonate, 822-38-8; tributylphosphine, 998-40-3.

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- When reaction is complete the mixture abruptly changes color from greenish-black to deep amber. If this change is not observed, additional drops of amine are added until it occurs.
- We are indebted to Dr. W. R. Hertler for this experiment.

Synthesis of Optically Active Sulfoximines from Optically Active Sulfoxides¹

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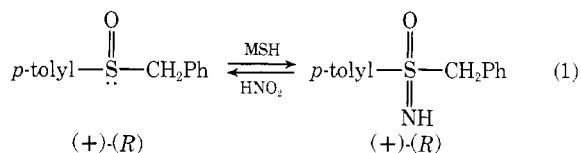
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Optically active sulfoximines are useful synthetic intermediates.² There are, however, only a few methods available for their preparation. One, involving resolution with

(+)-10-camphorsulfonic acid, has been found useful only in the case of *S*-phenyl-*S*-methylsulfoximine.^{3a,b} A resolution has been achieved by separation of *N*-(+)-10-camphorsulfonylsulfoximine diastereomers followed by removal of the resolving group by acid hydrolysis.^{3c} The reaction of an optically active sulfoxide with tosyl azide in the presence of copper catalyst⁴ results in optically pure *N*-tosylsulfoximines.^{3b} Hydrolysis with strong acid is required to remove the *N*-tosyl group; the hydrolysis often fails and/or results in extensive decomposition. The direct preparation of optically active "free" sulfoximines using the hydrazoic acid method⁵ is not applicable, since racemization of the starting sulfoxide occurs.^{3b} This note describes a simple one-step method for the production of optically active sulfoximines in good yield and high enantiomeric purity.

Reaction of *O*-mesitylsulfonylhydroxylamine (MSH) with sulfides and sulfoxides has been reported to produce sulfilmines and sulfoximines, respectively.⁶ In exploring the scope of this sulfoximine preparation we have found that the reaction of optically active sulfoxides with MSH results in sulfoximines of high optical purity. Table I shows the various optically active "free" sulfoximines prepared. By the nature of the various sulfoxides shown here and earlier⁶ it can be seen that the imidation reaction is quite general.

When 99% pure (+)-(*R*)-methyl *p*-tolyl sulfoxide was treated with MSH, (-)-(*R*)-*S*-methyl-*S*-*p*-tolylsulfoximine was obtained in 98.5% optical purity. Likewise, (-)-(*S*)-methyl phenyl sulfoxide with 94% optical purity was converted to (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine of 93.5% purity. Since the absolute configurations of these sulfoximines are known^{7,8} as well as the absolute configuration of the starting sulfoxides,^{9,10} it can be stated that these reactions occur with retention of configuration at the sulfur atom. Deimidation of (+)-benzyl-*p*-tolyl sulfoximine with nitrous acid (eq 1) resulted in (+)-benzyl *p*-tolyl



sulfoxide, which is known to have the *R* configuration.⁹ Cram and coworkers have shown this reaction to occur with retention of configuration.¹¹

Experimental Section

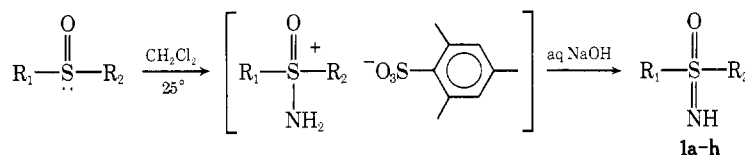
Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-dm cell.

The alkyl aryl and diaryl sulfoxides were obtained by the Anderson method in which the corresponding Grignard reagent was treated with (-)-menthyl *p*-toluenesulfinate;¹² for information concerning the assignment of their absolute configuration see ref 9. The preparation of (-)-(*R*)-methyl *n*-butyl sulfoxide as well as its configurational assignment has been described.¹³

O-Mesitylsulfonylhydroxylamine (MSH).¹⁴ Ethyl *O*-(mesitylsulfonyl)acetohydroxamate (7.5 g) was dissolved in dioxane (5 ml) and cooled to 0° with stirring. To this was added 70% perchloric acid (3 ml) dropwise at a rate so as to maintain the temperature below 10° . The resulting mixture was added to ice water (300 ml), the crude MSH was filtered off, washed well with water, and dissolved in ether (30 ml). The ether solution was washed with water (25 ml), treated with anhydrous potassium carbonate (5 g) for 30 sec and filtered. The ether solution was poured into cold pentane (300 ml) to precipitate the MSH as small crystals which were collected and dried under vacuum for 5 min at room temperature. Caution, this material may explode;¹⁵ it should be stored in a plastic container sealed with plastic or wax film.

Optically Active Sulfoximines. Compounds 1a-h were prepared by treating the corresponding optically active sulfoxide (2

Table I
Reactions of Sulfoxides with MSH



| R ₁ | R ₂ | Sulfoxide | | | Registry no. | Sulfonamide | | | Registry no. | |
|-------------------------------------------------|-------------------------------------------------|---------------------------------------------------|-------------------|-------------------|--------------|---------------------------------------------------|-------------------|-------------------|--------------|-------------------|
| | | [α] ²⁵ _D , deg (c, acetone) | Ab- solute config | Optical purity, % | | [α] ²⁵ _D , deg (c, acetone) | Ab- solute config | Optical purity, % | | Reaction yield, % |
| CH ₃ | <i>p</i> -Tolyl | +145.0 (1.00) | <i>R</i> | 99 | 1519-39-7 | -31.9 (3.00) | <i>R</i> | 98.5 | 80 | 20414-85-1 |
| C ₂ H ₅ | <i>p</i> -Tolyl | +188.0 (1.10) | <i>R</i> | 100 | 1519-40-0 | -22.9 (1.00) | <i>R</i> | 99 ^c | 70 | 51774-51-7 |
| CH(CH ₃) ₂ | <i>p</i> -Tolyl | +191.1 (1.255) | <i>R</i> | 100 ^a | 1517-74-4 | -17.1 (1.005) | <i>R</i> | 99 ^c | 79 | 51774-52-8 |
| (CH ₂) ₃ CH ₃ | <i>p</i> -Tolyl | +193.8 (1.430) | <i>R</i> | 100 ^b | 20288-49-7 | -17.2 (1.530) | <i>R</i> | 99 ^c | 77 | 51774-53-9 |
| C ₆ H ₅ CH ₂ | <i>p</i> -Tolyl | +234 (1.00) | <i>R</i> | 93 | 4820-07-9 | +4.7 (1.26) | <i>R</i> | 92 ^c | 60 | 51774-54-0 |
| C ₆ H ₅ | <i>p</i> -Tolyl | +21.0 (1.090) | <i>R</i> | 99.5 | 16491-20-6 | +5.0 (1.075) | <i>R</i> | 99 ^c | 19 | 51774-55-1 |
| C ₆ H ₅ | CH ₃ | -137.0 (1.20) | <i>S</i> | 94 | 18453-46-8 | +34.1 (2.00) | <i>S</i> | 93.5 | 70 | 33903-50-3 |
| CH ₃ | (CH ₂) ₃ CH ₃ | -110.3 (1.985) | <i>R</i> | 92 | 51795-48-3 | -5.00 (1.209) | <i>R</i> | 91.5 ^c | 78 | 51774-56-2 |

^a Highest rotation previously reported: +176.5° (ref 9). ^b Highest rotation previously reported: +187.0° (ref 9). ^c Assumed based on 99.5% retention of optical purity.

g) with a 40% excess of *O*-mesitylsulfonylhydroxylamine in methylene chloride (25 ml) at room temperature. After 2 hr the reaction mixture was poured into cold aqueous 10% NaOH (25 ml) solution, stirred for 10 min, and extracted with methylene chloride. The extracts were then washed with two 25-ml portions of 10% HCl solution and 5 ml of H₂O. If desired, unreacted sulfoxide (partially racemized) can be recovered by drying (MgSO₄) and concentrating the methylene chloride layer. Pure sulfonamide can be isolated as a colorless liquid or white solid by neutralizing the acidic aqueous layer with solid Na₂CO₃, extracting with methylene chloride, drying (MgSO₄), and concentrating. The solids were recrystallized from hexane.

Spectral data (ir and nmr) were consistent with the assigned structures. The most characteristic spectral feature indicative of the sulfonamide is noted in the infrared, where bands for the N-H (3270 cm⁻¹) and N=S=O (1110 and 1218 cm⁻¹) stretching are observed.

Registry No.—MSH, 36016-40-7.

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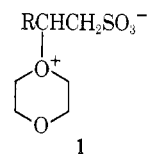
Sulfonation of 1-Butenes with Sulfur Trioxide

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The sulfonation of α-olefins can provide a variety of products ranging from sultones to alkanesulfonic acids¹ depending largely upon the sulfonating agent chosen. The reagents used most commonly are the sulfur trioxide-dioxane complex introduced by Suter² in 1938 and the sulfur trioxide-pyridine complex of Terent'ev,^{1,3} although very nearly the entire range of ethers and amines have been investigated. These complexes have sufficient activity to react with most organic substrates but reduce substantially the charring of products observed historically with sulfur trioxide. Unfortunately, yields are often quite low and serious side reactions from stabilization of intermediates by the complexing agent are encountered. For example, it has been suggested⁴ that dioxonium ions such as 1 are responsible for the formation of β-substituted al-



kanesulfonic acids in reactions of sulfur trioxide-dioxane with olefins. Attempts have been made to mitigate such complications by introducing sulfur trioxide as a gas, liquid, or solid⁵ to long-chain 1-olefins with no real success. We have found, however, that liquid sulfur trioxide introduced to a dilute solution of an olefin at -78° has none of the problems discussed and report here details of the synthesis of several 1,3-sultones in high yields. We also present evidence for the general mechanism of sulfonation of 1-olefins.

The addition of 1 equiv of liquid sulfur trioxide to 1-butenes in dichloromethane at -78° resulted in the formation of 1,3-propanesultones in at least 75% yield (Table I, examples 1, 3, 4, 5, and 6). Minor side products were 2-butene-1-sulfonic acids in 10-15% yield. An exception to