β-Keto Sulfoxides. II[1,2]

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The transformations summarized in Chart I have been achieved. The condensation products of esters and dimethyl sulfoxide can be converted to a variety of β-mercapto, β-methylsulfinyl, or β-methylsulfonyl ketones, alcohols, ethers, alkynes, alkenes, or alkanes.

The methylsulfinyl carbanion ($CH_3SOCH_2^-$), formed in dimethyl sulfoxide (DMSO) solutions of strong bases, has been shown to react with esters to give good yields of β-keto sulfoxides.[1,4] An analogous reaction of the methylsulfonyl carbanion ($CH_3SO_2CH_2^-$) yields the β-keto sulfones.[5]

$$CH_3SOCH_2^- + RCO_2R' \longrightarrow [RCOCHSOCH_3]^- \xrightarrow{H^+} RCOCH_2SOCH_3$$

β-Keto sulfoxides are not readily converted to β-keto sulfones since the conventional reagent for this transformation (acidic hydrogen peroxide) causes β-keto sulfoxides to undergo the Pummerer rearrangement to yield an α-keto hemimercaptal.[1] β-Keto sulfoxides

$$RCOCH_2SOCH_3 \xrightarrow{H^+} RCOCH(OH)SCH_3$$

or their Pummerer rearrangement products can be converted in high yield to a variety of sulfur-free products including α-keto esters, α-keto aldehydes, α-ketols, and methyl ketones. These transformations

$$RCO_2C_2H_5 \xrightarrow{CH_3SOCH_2^-} \longrightarrow \left\{ \begin{array}{l} RCOCH_3 \\ RCOCH_2OH \\ RCOCHO \\ RCOCO_2Et \end{array} \right.$$

will be described in a future publication.[6] At the present time we would like to report a variety of reactions in which the sulfur atom is retained. The major reactions investigated are summarized in Chart I.

β-Hydroxy sulfoxides (**3a**, **3b**) and β-hydroxy sulfones (**4a**) are readily prepared by the reduction of the β-keto sulfoxides (**1a**, **1b**) or β-keto sulfone (**2a**) with sodium borohydride in cold aqueous methanol. The reverse reactions are readily achieved by the use of active manganese dioxide.[7] β-Hydroxy sulfoxides and β-hydroxy sulfones have been prepared previously by the addition of the methylsulfinyl carbanion[7,8] or the methylsulfonyl carbanion,[9] or the corresponding Grignard reagents[9,10] to aldehydes or ketones, and by the autoxidation of mixtures of certain olefins and mercaptans.[11,12]

Reduction of β-keto sulfoxides **1a** and **1b** with lithium aluminum hydride yields the β-hydroxy sulfide (**5a**, **5b**). Compound **5a** can be oxidized to the β-hydroxy sulfoxide (**3a**) with sodium metaperiodate, or to the β-hydroxy sulfone (**4a**) with acidic hydrogen peroxide, or to the β-keto sulfide (**6a**) with active manganese dioxide. The β-keto sulfide (**6a**) can of course be easily prepared by the reaction of methyl mercaptide anion with phenacyl halides.

β-Hydroxy sulfoxides **3a** and **3b** upon treatment with sodium hydride in tetrahydrofuran react to form white solids which upon treatment with methyl iodide yield the corresponding β-methoxy sulfoxides, **7a** and **7b**. Similar treatment of β-hydroxy sulfide **5a** yields the β-methoxy sulfide (**8a**). However, treatment of the β-hydroxy sulfone **4a** with sodium hydride failed to form a salt and treatment of the reaction mixture with either water or methyl iodide before product isolation had no effect upon the product isolated, which has β-(methylsulfonyl)styrene (**10a**). Apparently the equilibrium between alkoxide anion and carbanion is such that elimination is greatly preferred for the β-hydroxy sulfone ($R = C_6H_5$).

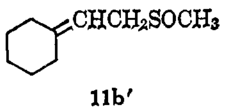
$$RCH(O^-)CH_2SOCH_3 \rightleftharpoons [RCH(OH)CHSOCH_3]^-$$

$$RCH(O^-)CH_2SO_2CH_3 \rightleftharpoons [RCH(OH)CHSO_2CH_3]^- \longrightarrow RCH{=}CHSO_2CH_3 + OH^-$$

Treatment of the β-hydroxy sulfone (**4a**) or β-hydroxy sulfoxide (**3a**) with phosphoric acid resulted in the formation of the unsaturated sulfone (**10a**) and unsaturated sulfoxide (**11a**), respectively. Apparently only a single isomer (*trans*) was formed. The olefinic hydrogens had coupling constants of $J_{AB} = 15.6$ cps in both cases. Distillation of the β-hydroxy sulfide (**5a**) from potassium bisulfate yielded the unsaturated sulfide **12a** as a mixture of *trans* (predominant), $J_{AB} = 15.8$ cps, and *cis* (minor), $J_{AB} = 11$ cps, isomers.

Attempts to prepare **9a** by oxidation of **7a** with acidic hydrogen peroxide gave rise to mixtures of **9a** and **10a**. Evidently **9a** is very sensitive to the elimination of methanol under either acidic or basic conditions.

Treatment of **7a** with sodium hydride followed by heating in tetrahydrofuran solution gives rise to β-(methylsulfinyl)styrene (**11a**). Treatment of **7b** under identical conditions yielded the β,γ unsaturated sulfoxide, ω-(methylsulfinylmethyl)methylenecyclohexane (**11b[1]**). This result is in agreement with the results of



11b′

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[1] For part I, see H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963).

[2] Supported by a grant from the Army Office of Research (Durham).

[3] National Science Foundation Cooperative Fellow, 1964–1966.

[4] (a) E. J. Corey and M. J. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1639 (1964); **87**, 1345 (1965); (b) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963).

[5] H.-D. Becker and G. A. Russell, *ibid.*, **28**, 1896 (1963).

[6] Unpublished results of Dr. G. J. Mikol.

[7] G. A. Russell and H.-D. Becker, *J. Am. Chem. Soc.*, **85**, 3406 (1963).

[8] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962); G. A. Russell, E. G. Janzen, H.-D. Becker, and F. J. Smentowski, *ibid.*, **84**, 2652 (1962).

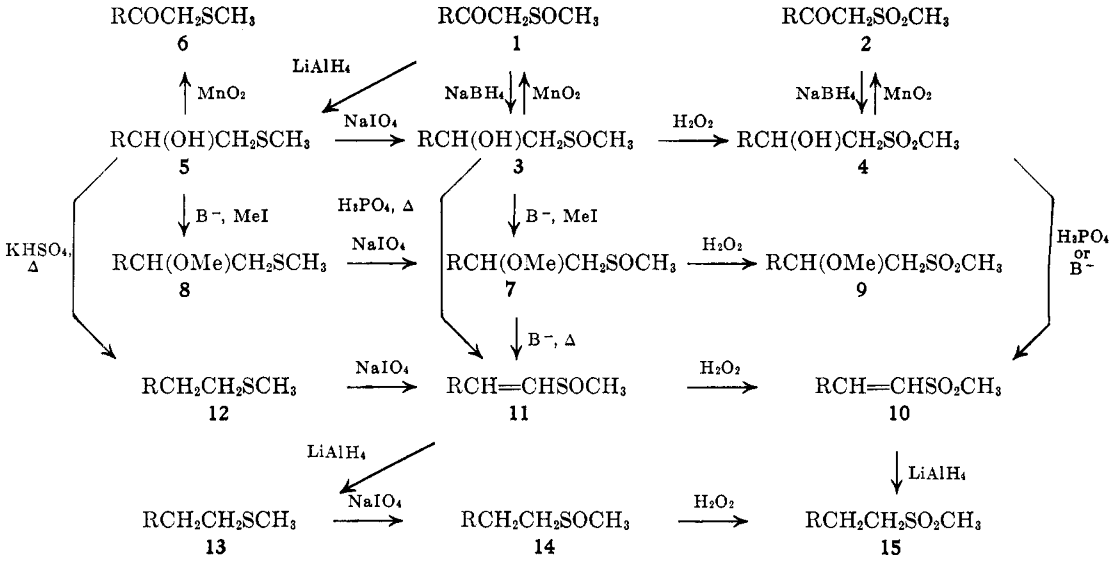
[9] W. E. Truce and K. R. Buser, *ibid.*, **76**, 3577 (1954).

[10] L. Field, *ibid.*, **74**, 3919 (1952); L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

[11] M. S. Kharasch, W. Nudenberg, and G. J. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

[12] H. H. Szmantand R. L. Lapinski, *ibid.*, **21**, 847 (1956).

Chart I
Reactions of β-Keto Sulfoxides



a, R = phenyl; **b**, R = cyclohexyl

O'Connor and Lyness who have shown that basic solutions of unsaturated sulfoxides upon equilibration form the β,γ isomers.[13] The unsaturated sulfide **12a** is readily oxidized to the unsaturated sulfoxide (**11a**) or sulfone (**10a**).

Reduction of the unsaturated sulfoxide **11a** with lithium aluminum hydride gave the saturated sulfide **13a** which could be oxidized to β-(methylsulfinyl)-ethylbenzene (**14a**) or β-(methylsulfonyl)ethylbenzene (**15a**). The latter compound can also be prepared by the lithium aluminum hydride reduction of the unsaturated sulfone (**10a**).

β-Hydroxy sulfoxides or vinyl sulfoxides can be converted to the acetylenic sulfides. Treatment of **3a** with thionyl chloride yields a chlorostyrenyl sulfide (from pmr) which can be dehydrohalogenated with alcoholic potassium hydroxide to yield methyl phenethynyl sulfide in a 63% over-all yield.

$$\mathbf{3a} + SOSl_2 \longrightarrow [C_6H_5CH(Cl)CH_2SOCH_3] \longrightarrow$$
$$\mathbf{11a} \xrightarrow{SOCl_2} C_6H_5C(Cl){=}CHSCH_3 \xrightarrow[C_2H_5OH]{KOH} C_6H_5C{\equiv}CSCH_3$$

Evidence for the proposed reaction scheme is furnished by the observation that **11a** reacts with thionyl chloride to yield the methyl chlorostyrenyl sulfide in high yield.

The intermediate methyl chlorostyrenyl sulfide could not be obtained in a highly purified state. Four isomeric structures are possible (*cis, trans*, α-chloro, β-chloro) and in some samples four methyl singlets in pmr could be detected although one singlet greatly predominated (2.41 ppm). However all samples gave only a single sharp vinyl proton at 6.57 ppm. The predominant structure of the methyl chlorostyrenyl sulfide was proven as α-chloro-β-(methylmercapto)-styrene by the observation that β-phenyl-β-deuterioxy-α,α-dideuterioethyl methyl sulfoxide ($C_6H_5CH(OD)CD_2SOCH_3$) reacted with thionyl chloride to give a methyl chlorostyrenyl sulfide without any absorption by a vinyl hydrogen atom in pmr.

$$C_6H_5CH(OD)CD_2SOCH_3 + SOCl_2 \longrightarrow C_6H_5C(Cl){=}CDSCH_3 + SO_2 + 2DCl + HCl$$

Treatment of β-deuterio-β-(methylsulfinyl)styrene with thionyl chloride yielded a methyl chlorostyrenyl with 0.2 of a vinyl hydrogen atom absorbing at 6.57 ppm. Apparently, the major reaction is to yield the α-chloro-β-(methylmercapto)styrene.

$$C_6H_5CH{=}CDSOCH_3 + SOCl_2 \longrightarrow C_6H_5C(Cl){=}CDSCH_3 + SO_2 + HCl$$

However, the hydrogen chloride formed partially exchanges with the deuterium atom in β-deuterio-β-(methylsulfinyl)styrene.

$$C_6H_5CH{=}CDSOCH_3 + HCl \longrightarrow C_6H_5CH{=}CDSOCH_3 + DCl$$

Such exchange is not experimentally observed starting from the α,α-dideuterio-β-deuterioxy sulfoxide because the reaction with thionyl chloride produces two moles of deutrium chloride to 1 mole of hydrogen chloride. The reaction of thionyl chloride with β-(methylsulfinyl)styrene gave only tars in pyridine solution.

From the above observations it is obvious that transition state A is preferred to B or C in the reaction of the unsaturated sulfoxide with thionyl chloride. The preference of A over B or C may be due to steric effects in the nonplanar transition state or due to the stability of the reaction products.

$$A \longrightarrow ArCH(Cl)CH{=}\overset{+}{S}{-}CH_3$$
$$B \text{ or } C \longrightarrow Ar\overset{+}{C}H{-}CH(Cl)SCH_3$$

Pyrolysis of the β-hydroxy sulfoxides **3a** and **3b** yielded acetophenone and acetylcyclohexane, respectively.

$$RCH(OH)CH_2SOCH_3 \xrightarrow{\Delta} RCOCH_3 + CH_3SOH$$

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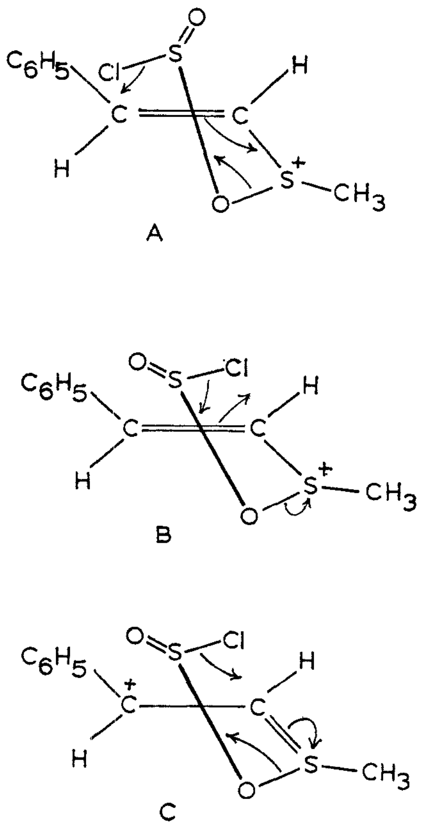
[13] D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85**, 3044 (1963); **86**, 3840 (1964); D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964).



Transition States

Acetylcyclohexane can also be formed from **5b** by heating in the presence of a trace of dicumyl peroxide, presumably *via* the following reaction sequence.[14]

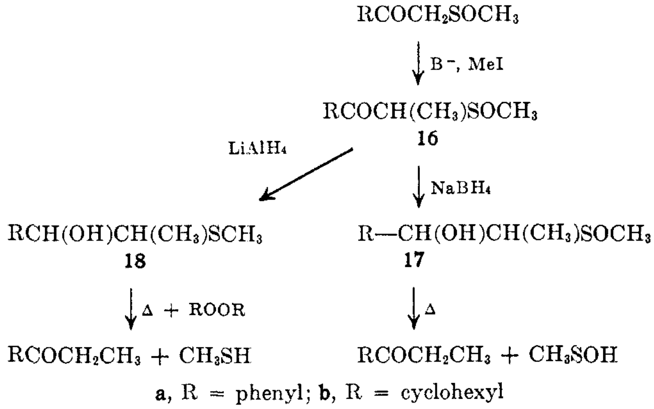
$$\text{dicumyl peroxide} \xrightarrow{\Delta} \text{C}\cdot$$

$$\text{C}\cdot + \text{RCH(OH)CH}_2\text{SCH}_3 \longrightarrow \text{CH} + \text{R}\dot{\text{C}}\text{(OH)CH}_2\text{SCH}_3 \longrightarrow \text{RC(OH)}{=}\text{CH}_2 + \text{CH}_3\text{S}\cdot$$

$$\text{CH}_3\text{S}\cdot + \text{RCH(OH)CH}_2\text{SCH}_3 \longrightarrow \text{CH}_3\text{SH} + \text{R}\dot{\text{C}}\text{H(OH)CH}_2\text{SCH}_3$$

These results suggested that the corresponding vinyl ethers could be prepared by subjecting the corresponding methyl ethers (**7a, b** and **8a, b**) to pyrolysis and free radial sources, respectively. However, pyrolysis of **7a** has so far yielded mainly the unsaturated sulfoxide **11a**.

The synthetic utility of β-keto sulfoxides is significantly enhanced by the fact that the methylene group α to both the carbonyl and sulfoxide function can be alkylated in high yield.



a, R = phenyl; **b**, R = cyclohexyl

Formation of propiophenone in 67% yield from **18a** has been achieved. Considerable lower yields of propiophenone (~30%) have been observed in the pyrolysis of **17a**. The conversions of **17b** and **18b** to ketones has not yet been achieved by these routes.

Experimental Section

Reagents.—Dimethyl sulfoxide (DMSO) was dried over calcium hydride and distilled under vacuum. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Sodium hydride was used as a 50% suspension in mineral oil obtained from Metal Hydrides, Inc. The mineral oil was removed by washing with Skellysolve A prior to use.

Preparation of β-Keto Sulfoxides.—ω-(Methylsulfinyl)acetophenone, **1a**, and ω-(methylsulfinyl)acetylcyclohexene, **1b**, were prepared as previously reported.[1,4]

β-Hydroxy-β-phenethyl Methyl Sulfoxide, 3a.—Compound **1a** (30 g) was dissolved in 100 ml of water and cooled in an ice bath. While stirring with a magnetic stirrer, sodium borohydride (1.70 g) in 10 ml of water was added slowly. After stirring for 2 hr the solution was thoroughly extracted with chloroform. The extracts were dried over magnesium sulfate and filtered. Evaporation of the solvents left a colorless oil which after the removal of the final traces of solvent at 1 mm crystallized in colorless needles (29.9 g, 98%) melting at 78–123°. Recrystallization from ethyl acetate did not effect separation of the diastereomers. The infrared spectrum was superimposable with an authentic sample prepared by addition of methylsulfinyl carbanion to benzaldehyde.[7]

β-Hydroxy-β-cyclohexylethyl Methyl Sulfoxide, 3b.—By the same procedure used to prepare **3a**, compound **1b** (2.04 g) gave **3b** (1.98 g, 97%) as a white solid. Recrystallization from isopropyl ether permitted separation into two pairs of isomers, the more soluble isomer melting at 50–52° and the more insoluble isomer melting at 94–96°. The sample for analysis was not separated into diastereomers.

Anal. Calcd for $C_9H_{18}O_2S$: C, 56.82; H, 9.54; S, 16.82. Found: C, 57.02; H, 9.55; S, 16.83.

β-Hydroxy-β-phenethyl Methyl Sulfone, 4a.—By the same procedure used to prepare **3a**, compound **2a** (9.10 g) gave **4a** (7.89 g 86%) as colorless crystals melting at 102–104°. Recrystallization from benzene–carbon tetrachloride mixture raised the melting point to 105–106° (lit.[9] mp 106–106.5°).

β-Hydroxy-β-phenethyl Methyl Sulfide, 5a.—A solution of **1a** (20.0 g, 110 mmoles) in 200 ml of THF was added dropwise to lithium aluminum hydride (6.5 g) suspended in THF at a rate sufficient to maintain reflux. The mixture was refluxed for 24 hr, cooled, and diluted carefully with 100 ml of water. The hydroxides which formed were dissolved with hydrochloric acid. The aqueous solution was extracted with chloroform. The combined extracts were dried over magnesium sulfate and filtered. Removal of the solvent left a yellow liquid which was distilled at 1 mm. A fraction boiling at 92–95° (13.54 g, 73%) was collected (lit.[15] bp 142–143° at 15 mm). The methiodide derivative was prepared, mp 137–139° (lit.[16] mp 133–134°).

β-Hydroxy-β-cyclohexylethyl Methyl Sulfide, 5b.—When **1b** (9.90 g) was treated in a manner used to prepare **5a**, the product **5b** (6.54 g, 75%) was obtained as the fraction boiling at 92° at 1 mm.

Anal. Calcd for $C_9H_{18}OS$: C, 62.04; H, 10.41; S, 18.37. Found: C, 61.93; H, 10.36; S, 18.29

β-Hydroxy-β-phenethyl Methyl Sulfoxide, 7a.—Compound **3a** (9.20 g, 50 mmoles) in 100 ml of THF was added to a suspension of sodium hydride (1.10 g) in 25 ml of THF at such a rate that refluxing did not occur. Excess methyl iodide was added. The mixture was stirred for 3 hr at 25°. The reaction mixture was then added carefully to 500 ml of water. The aqueous mixture was extracted with chloroform. The combined extracts were dried over magnesium sulfate and filtered. Removal of the solvents left a light yellow oil which was vacuum distilled. The fraction boiling at 135–137° at 1 mm (6.48 g, 72%) was collected.

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.59; H, 7.12; S, 16.14. Found: C, 60.38; H, 7.13; S, 16.07.

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[14] This reaction was suggested to us by Dr. E. S. Huyser.

[15] T. Yamanashi, Y. Obata, and M. Sano, *J. Agr. Chem. Soc., Japan*, **26**, 125 (1952); *Chem. Abstr.*, **46**, 2301*a* (1958).

[16] V. Prelog, V. Hahn, H. Brauchli, and H. C. Beyerman, *Helv. Chim. Acta*, **27**, 1209 (1944).

β-Methoxy-β-cyclohexylethyl Methyl Sulfoxide, 3b.—By repetition of the procedure used to prepare **7a**, compound **1b** (5.10 g) produced compund **3b** (3.95 g, 72%) as a mixture of the diastereomers boiling at 118–139° at 0.5 mm.

Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.80; H, 9.87; S, 15.67. Found: C, 58.67; H. 9.76; S, 15.80.

β-Methoxy-β-phenethyl Methyl Sulfide, 8a.—In the manner used to prepare **7a**, compound **5a** (20.1 g) produced **8a** (17.17 g, 81%) boiling at 86–91° at 2 mm.

β-Methoxy-β-cyclohexylethyl Methyl Sulfide, 8b.—In the manner used to prepare **7a**, compound **5b** (4.90 g) produced **8b** (3.40 g, 65%) boiling at 49–54° at 0.10–0.15 mm.

Anal. Calcd for $C_{10}H_{20}OS$: C, 63.79; H, 10.71; S, 17.00. Found: C, 63.92; H, 10.54; S, 16.87.

β-(Methylsulfinyl)styrene, 11a.—Compound **7a** (1.98 g) in 25 ml of THF was added to a suspension of sodium hydride (0.36 g, 15 mmole) in 25 ml of THF. The mixture was refluxed for 1 hr and then poured into water. The aqueous solution was extracted with chloroform. The combined extracts were dried over magnesium sulfate and filtered. Removal of the solvent left **7a** (1.64 g, 100%) as a slightly yellow solid, mp 45–50°. Recrystallization from ether raised the melting point to 61–62°.

Anal. Calcd for $C_9H_{10}OS$: C, 65.05; H, 6.07; S, 19.26. Found: C, 65.21; H, 6.14; S, 19.20.

The 60-Mcps pmr resonance showed an AB quartet for the olefinic hydrogens, $\delta_A = 7.20$, $\delta_B = 6.91$ ppm, $J_{AB} = 15.5$ cps.

ω-(Methylsulfinylmethyl)methylenecyclohexane, 11b′.—When compound **7b** (4.08 g) was treated with base as in the above procedure, **11b′** (3.4 g, 100%) was obtained as a pasty semi-solid. Recrystallization from ethyl acetate gave a white solid, mp 38–39°. The material may also be distilled at 92–94° at 0.1 mm.

Anal. Calcd for $C_9H_{16}OS$: C, 62.76; H, 9.36; S, 18.58. Found: C, 62.66; H, 9.29; S, 18.61.

The pmr spectrum showed one olefinic proton as a triplet centered at δ 5.13 ($J = 8$ cps) and the methylene protons as a doublet at δ 3.35 ($J = 8$ cps).

Methyl β-Styryl Sulfide, 12a.—Potassium hydrogen sulfate (50 g) was placed in a flask equipped with a pressure compensating addition funnel and a distillation head. The temperature was raised to 230° and the pressure was reduced to 0.3 mm. After 1 hr **5a** (11.56 g) was added dropwise. The dark brown distillate was taken up in ether, dried over magnesium sulfate, and filtered through charcoal. Removal of the solvent gave 5.23 g of a light yellow liquid. The liquid was fractionally distilled and the fraction boiling at 110–113° at 3 mm (3.96 g, 38%) was collected. The pmr spectrum showed the olefinic protons as a quartet, $J_{AB} = 15.8$ cps, $\delta_A = 6.66$, $\delta_B = 6.18$ ppm. A low-intensity quartet, $J_{AB} = 11.0$ cps, $\delta_A = 6.32$, $\delta_B = 6.02$ ppm, indicates the presence of a trace of the *cis* olefin. The *cis* olefin is reported to boil at 100–105° (4 mm).[17]

β-(Methylsulfonyl)styrene, 10a.—Compound **4a** (5.00 g) in 100 ml of THF was added to a suspension of sodium hydride (2.56 g, 100 mmoles) in 25 ml of THF. The mixture was refluxed for 1 hr and then poured into water. The aqueous solution was extracted with chloroform. The combined extracts were dried over magnesium sulfate and filtered. Removal of the solvent gave **10a** (3.42 g, 74%) as a pasty solid. Recrystallization from aqueous ethanol raised the melting point to 78–79°. A mixture melting point with an authentic sample prepared by phosphoric acid catalyzed dehydration of **4a** showed no depression. The pmr spectrum showed an AB quartet with $\delta_A = 7.66$, $\delta_B = 6.99$ ppm, and $J_{AB} = 15.5$ cps.

β-Phenethyl Methyl Sulfide, 13a.—When **11a** (0.85 g) was refluxed with lithium aluminum hydride in THF the product obtained was **13a** (0.6 g, 82%), bp 65–67° (1 mm). Proof of structure was obtained by the integrated pmr spectrum and by oxidation to the known sulfone, mp 83–85° (lit.[18] mp 85–86°).

β-Phenethyl Methyl Sulfone, 15a.—When compound **10** (5.00 g) was refluxed with lithium aluminum hydride the product obtained was **15a** (2.80 g, 55%), mp 86–77° after recrystallization from methanol (lit.[18] mp 85–86°).

Sodium Metaperiodate Oxidations.—All of the metaperiodate reactions were carried out essentially by the method of Leonard and Johnson.[19]

Compound **5a** (500 mg) when treated with sodium metaperiodate gave a light yellow solid. Recrystallization from ethyl acetate gave pure **2a** (410 mg, 75%). The infrared spectrum was superimposable with **2a** prepared by sodium borohydride reduction of **1a**.

Compound **8a** (5.46 g) when oxidized by sodium metaperiodate produced **7a** (5.35 g, 90%). The infrared spectrum was superimposable with **7a** produced by methylation of **3a**.

Compound **12a** (500 mg) when oxidized by sodium metaperiodate produced **11a** (424 mg, 77%). The infrared spectrum was superimposable with **11a** produced by treatment of **7a** with base. A mixture melting point showed no depression.

Compound **13a** (1.00 g) when oxidized with sodium metaperiodate produced **14a** (0.79 g, 72%) as a colorless oil.

Anal. Calcd for $C_9H_{12}OS$: C, 64.27; H, 7.19; S, 19.03. Found: C, 64.17; H, 6.97; S, 19.19.

Hydrogen Peroxide Oxidations.—In all reactions the material to be oxidized was dissolved in a minimal amount of glacial acetic acid. Excess hydrogen peroxide was added, and the reaction mixture was warmed on a steam bath for 30 min. The mixture was then diluted with an equal volume of water and cooled. If crystallization did not take place the solution was neutralized with sodium bicarbonate solution and extracted with chloroform. After drying the extracts over magnesium sulfate the solvent was removed to give the product.

Compound **3a** (10.0 g) when treated with acidic hydrogen peroxide gave **4a** (9.02 g, 83%), mp 102–104°. The infrared spectrum was superimposable with **4a** produced by sodium borohydride reduction of **2a**.

Compound **11a** (1.00 g) when treated with acidic hydrogen peroxide gave **10a** (0.93 g, 85%), mp 67–70°. Recrystallization from aqueous–ethanol raised this to mp 77–79°. The infrared spectrum was superimposable with **10a** produced by acid- and base-catalyzed dehydration of **4a**.

Compound **14a** (501 mg) when treated with acidic hydrogen peroxide gave **15a** (492 mg, 89%). The infrared spectrum was identical with **15a** produced by lithium aluminum hydride reduction of **10a**.

Manganese Dioxide Oxidations.—The use of manganese dioxide to oxidize β-hydroxy sulfoxides to β-keto sulfoxides has been reported previously.[7] The same procedure was used to oxidize the analogous β-hydroxy sulfides and sulfones.

Compound **5a** (123 mg) when oxidized with manganese dioxide gave **6a** (99 mg, 82%). The infrared spectrum was superimposable with that of an authentic sample prepared from ω-bromoacetophenone and methyl mercaptan.

Compound **4a** (100 mg) when oxidized with manganese dioxide gave **2a** (89 mg), mp 97–100°. Recrystallization from a chloroform–ethanol mixture raised the melting point to 104–106°. A mixture melting point with an authentic sample showed no depression.

Pyrolysis Reactions.—The material to be pyrolyzed was placed in a small flask equipped with a reflux condenser. The flask was then immersed in a metal bath at 230–240° for 15 min. The pyrolysate was then either chromatographed on silica gel or taken up in ethanol, filtered through charcoal, and treated with 2,4-dinitrophenylhydrazine. The results are shown in Table I.

TABLE I

PYROLYSIS OF β-HYDROXY SULFOXIDES

Material pyrolyzed	Product	Yield, %
$C_6H_5CH(OH)CH_2SOCH_3$	$C_6H_5COCH_3$	77
$C_6H_{11}CH(OH)CH_2SOCH_3$	$C_6H_{11}COCH_3$	26
$C_6H_5CH(OH)CH(CH_3)SOCH_3$	$C_6H_5COCH_2CH_3$	29
$C_6H_{11}CH(OH)CH(CH_3)SOCH_3$	$C_6H_{11}COCH_2CH_3$	Trace

Dicumyl Peroxide Reactions.—The substrate was placed in a small flask equipped with a reflux condenser. Approximately 0.1 equiv of dicumyl peroxide was added, and the flask was immersed in an oil bath (150–155°) for 24 hr. The stench of methyl mercaptan immediately became noticeable. The mixture was then fractionally distilled through a Vigreux column. The results are summarized in Table II.

ω-Methyl-ω-(methylsulfinyl)acetophenone, 16a.—Sodium hydride (0.50 g) was slurried with 50 ml of THF. While stirring, **1a** (3.64 g) in 100 ml of THF was added dropwise. A white solid formed immediately. Fifteen minutes after addition was complete, excess methyl iodide was added and the mixture was allowed to stir at room temperature for 3 hr. The reaction mix-

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[17] W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956).

[18] W. E. Bacon and W. M. LeSuer, *ibid.*, **76**, 670 (1954).

[19] N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962); N. J. Leonard and C. R. Johnson, *J. Am. Chem. Soc.*, **84**, 3701 (1962).

TABLE II

DECOMPOSITION OF β-HYDROXY SULFOXIDES BY FREE-RADICAL MECHANISM

Substrate (mmoles)	Peroxide, mmoles	Product[a]	Yield, mmoles (%)
$C_6H_5CH(OH)CH_2SCH_3$ (20.6)	2.9	$C_6H_5COCH_3$	19.0 (93)
$C_6H_{11}CH(OH)CH_3SCH_3$ (36.4)	3.5	$C_6H_{11}COCH_3$	29.8 (82)
$C_6H_5CH(OH)CH(CH_3)$-SCH_3 (21.5)	2.9	$C_6H_5COCH_2CH_3$	14.8 (67)
$C_6H_{11}CH(OH)CH(CH_3)$-SCH_3 (15.8)	1.8	$C_6H_{11}COCH_2CH_3$	Trace

[a] Some acetophenone was found in all cases, presumably due to decomposition of dicumyl peroxide.

ture was poured into 400 ml of water containing a few crystals of sodium thiosulfate. The aqueous solution was extracted thoroughly with chloroform. The combined extracts were dried magnesium sulfate and filtered. Removal of the solvent gave **16a** (3.95 g, 100%) as a light yellow oil shown by pmr to be an equal mixture of the expected diastereomers. Upon cooling in an ice bath one of the diastereomers crystallized. Washing with ether gave a white solid, mp 74–75°.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.21; H, 6.17; S, 16.31. Found: C, 61.23; H, 6.19; S, 16.19.

α-(Methylsulfinyl)ethyl Cyclohexyl Ketone, 16b.—In a manner similar to the preparation of **16a**, **1b** (7,80 g) produced **16b** (8.40 g, 101%). Here again crystallization of one diastereomer was effected, mp 36–40°.

Anal. Calcd for $C_{10}H_{18}O_2S$: C, 59.38; H, 8.97; S, 15.82. Found: C, 59.39; H, 8.95; S, 15.84.

1-Hydroxy-1-phenyl-2-propyl Methyl Sulfide, 18a.—Compound **16a** (18.2 g), when treated with lithium aluminum hydride in the same manner as for the conversion of **1a** to **5a**, produced **18a** (12.8 g, 69%), bp 105–106° at 0.5 mm.

Anal. Calcd for $C_{10}H_{14}OS$: C, 65.91; H, 7.74; S, 17.56. Found: C, 66.02; H, 7.69; S, 17.48.

1-Cyclohexyl-1-hydroxy-2-propyl Methyl Sulfide, 18b.—Compound **16b** (9.40 g) when treated with lithium aluminum hydride produced **18b** (6.27 g, 72%), bp 86–88° at 0.5 mm.

Anal. Calcd for $C_{10}H_{20}OS$: C, 63.79; H, 10.71; S, 17.00. Found: C, 63.83; H, 10.64; S, 16.94.

1-Phenyl-2-(methylsulfinyl)propanol, 17a.—Compound **16a** (19.8 g) when reduced with sodium borohydride gave **17a** (19.7 g, 98%) as a light yellow oil which crystallized after standing for 3 weeks, mp 79–101° after recrystallization from ethyl acetate.

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.59; H, 7.12; S, 16.15. Found: C, 60.37; H, 7.27; S, 16.29.

1-Cyclohexyl-2-(methylsulfinyl)propanol, 17b.—Reduction with sodium borohydride of **16b** (3.76 g) gave **17b** (3.73 g, 98%).

Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.80; H, 9.87; S, 15.67. Found: C, 58.71; H, 9.73; S, 15.64.

Methyl Phenethynyl Sulfide.—Compound **3a** (46 g) in 200 ml of methylene chloride was added dropwise to thionyl chloride (118 g) in 200 ml of methylene chloride. The mixture was stirred for 10 hr. The solvent and the excess thionyl chloride were removed on a steam bath. The residue was distilled under reduced pressure, 108–114° at 0.5–1.0 mm, to give 39 g of light yellow liquid. This was dissolved in 150 ml of absolute ethanol and added dropwise to potassium hydroxide (29 g) in 100 ml of absolute ethanol. The mixture was refluxed overnight. After filtering the solvent was removed at aspirator pressure. The product (23.2 g, 63%) was distilled at 85–87° (2 mm) [lit.[20] bp 74° (2 mm)].

The infrared spectrum shows an acetylene absorption, ν_{CCl_4} 2160 cm^{-1}. The pmr spectrum in carbon tetrachloride consists of an aromatic multiplet (δ = 7.1–7.5 ppm) and a singlet (δ = 2.38 ppm) with relative areas 5 to 3.

Methyl phenethynyl sulfide could also be prepared by reaction of β-(methylsulfinyl)styrene with thionyl chloride. The same intermediate chlorostyrenyl sulfide was produced as formed in the reaction of thionyl chloride with **3a**. The intermediate chlorostyrenyl sulfide had a single vinyl hydrogen at δ = 6.57 ppm and gave olefinic absorption, ν_{CCl_4} 1665 cm^{-1}.

ω,ω-Dideuterio-ω-(methylsulfinyl)acetophenone.—Compound **1a** was dissolved in deuterium oxide containing a trace of potassium carbonate. After stirring for 1 hr the solution was thoroughly extracted with chloroform, dried over magnesium sulfate, and filtered. Removal of the solvent gave a white solid, mp 83–84.5°. The pmr spectrum showed only a methyl singlet and aromatic multiplets at δ = 7.3–7.7 and 7.9–8.1 ppm.

β-Phenyl-β-deuterioxy-α,α-dideuterioethyl Methyl Sulfoxide.—Sodium borohydride reduction of ω,ω-dideuterio-ω-(methylsulfinyl)acetophenone in deuterium oxide gave a 97% yield of β-phenyl-β-deuterioxy-α,α-dideuterioethyl methyl sulfoxide as a mixture of diastereomers. The pmr spectrum showed only methyl absorptions, δ = 2.48 and 2.56, methine absorption, 5.18, and aromatic absorption, 7.33 ppm.

β-Deuterio-β-(methylsulfinyl)styrene.—Treatment of β-phenyl-β-deuterioxy-α,α-dideuterioethyl methyl sulfoxide (3.00 g) with excess sodium hydride and methyl iodide as in the preparation of **11a** produced β-deuterio-β-(methylsulfinyl)styrene (2.08 g), mp 62–63°. The pmr showed a methyl absorption, δ = 2.59, one olefinic proton, 7.08, and aromatic absorption, 7.2–7.6 ppm.

α-Chloro-β-deuterio-β-(methylmercapto)styrene.—Treatment of either β-phenyl-β-deuterioxy-α,α-dideuterioethyl methyl sulfoxide or β-deuterio-β-(methylsulfinyl)styrene with thionyl chloride produced predominantly α-chloro-β-deuterio-β-(methylmercapto)styrene. The pmr spectrum showed a methyl absorption, δ = 2.41, and aromatic absorption, 7.2–7.6 ppm. In the β-deuterio-β-(methylsulfinyl)styrene case some exchange occurred as evidenced by olefinic absorption at 6.57 ppm which integrated to less than 0.2 of a proton based on the integration of the methyl peak. The α-chloro-β-deuterio-β-(methylmercapto)styrene produced from β-phenyl-β-deuterioxy-α,α-dideuterioethyl methyl sulfoxide did not show any absorption by olefinic protons in pmr.

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[20] M. Schmidt and V. Potschka, *Naturwissenschaften*, **50**, 302 (1963).