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Synthesis of Alkenes by Reductive Elimination of β-Hydroxysulfoximines

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Abstract: β-Hydroxysulfoximines, obtained in high yield by the addition of α-lithio derivatives of *S*-alkyl-*N*-methyl-*S*-phenylsulfoximines to aldehydes and ketones, undergo reductive elimination to yield alkenes upon treatment with aluminum amalgam in a mixture of tetrahydrofuran, water, and acetic acid. Dienes and trienes were obtained from enones and dienones, respectively. Diastereomers of 5-(*N*-methylphenylsulfonimidoyl)-4-octanol were prepared in stereochemically pure forms; reductive elimination of each diastereomer gave rise to a mixture of *cis*- and *trans*-4-octene (60–84% trans). β-Hydroxy sulfides, sulfoxides, and sulfones do not eliminate under comparable conditions. A 1,3 elimination did not occur when 3-(*N*-methylphenylsulfonimidoyl)-1-phenyl-1-propanol was treated with aluminum amalgam; the reaction gave 1-phenyl-1-propanol.

The transformation of a carbonyl group to a carbon–carbon double bond, a reaction of broad significance, has received considerable attention in the chemical literature. Foremost among the methods available for effecting this transformation is the reaction of an aldehyde or ketone with a phosphorus ylide. Known as the Wittig reaction, this procedure is uncommonly versatile and has been extensively employed in synthetic chemistry.[1] Nevertheless, it has its limitations and alternative methods have been and will continue to be developed.

The use of sulfur-derived reagents to effect the methylenation of carbonyl compounds is a relatively recent innovation and in most instances has not proven to be as general or as simple as the Wittig reaction. (Sulfur ylides that are analogous to the Wittig reagent react with carbonyl compounds to give oxiranes, not alkenes.)[2] Corey has introduced a method of carbonyl methylenation involving β-hydroxysulfinamides which thermally decompose to yield alkenes.[3] The β-hydroxysulfinamides in turn are derived from the reaction of *N*-*p*-tolylmethanesulfinamide dianion with an aldehyde or ketone. Durst has developed an interesting and general procedure for carbonyl methylenation that is based upon β-hydroxy sulfoxides.[4] It was found that the β-hydroxy sulfoxides derived from a carbonyl compound and the anion of a *tert*-butyl alkyl sulfoxide undergo reaction with positive halogen to yield alkenes. Overall yields for this procedure are high; the reaction appears to be quite general. The use of positive halogenating agents precludes the presence of sensitive functionality in the molecule.

Reductive elimination of sulfur-containing molecules is a recent innovation in this field. Coates has shown that the *O*-acetates or benzoates of β-hydrosulfides undergo reductive elimination in the presence of dissolving alkali metals to yield alkenes.[5] β-Hydroxy sulfides also yield alkenes by electroreduction.[6] A similar procedure has recently appeared that involves the use of 2-methylthiopyridine, which is reacted as its anion with a carbonyl compound to yield a β-hydroxy sulfide.[7] This, on successive treatment with titanium tetrachloride, ammonia, and zinc, undergoes reductive elimination to yield an alkene. A methylenation procedure based on the reductive elimination of β-hydroxy sulfones has been described by Julia.[8] The β-hydroxy sulfones (derived from the reaction of anions of alkyl phenyl sulfones with carbonyl compounds), upon reduction with sodium amalgam in ethanol, give rise to alkenes. Where geometric isomers are possible, the reaction produces equal amounts of cis and trans alkenes.[9]

Several intriguing procedures based on 1,2 eliminations initiated by treatment of sulfur-containing substrates with tin hydrides have been described recently;[10,11] these eliminations apparently proceed by a radical mechanism. In the present paper we present a procedure for the reductive elimination of β-hydroxysulfoximines which we believe offers experimentalists a useful method for achieving methylenation of carbonyl compounds. The method is based on the readily available *S*-alkyl-*N*-methyl-*S*-phenylsulfoximines.[12]

Results and Discussion

(*N*-Methylphenylsulfonimidoyl)methyllithium (**2**), gen-

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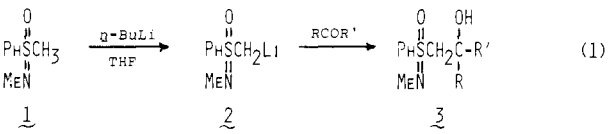

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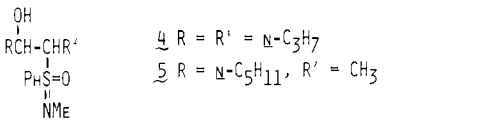
erated by reaction of **1**[13] with butyllithium, readily adds to aldehydes and ketones to yield β-hydroxysulfoximines (**3**). We have shown that aluminum amalgam in aqueous tetrahydrofuran (THF) is capable of effecting a reductive cleavage of the alkyl carbon–sulfur bond in selected β-hydroxysulfoximines to yield alcohols.[13] We envisioned an alkene synthesis based on the reduction–elimination of sulfoximines possessing leaving groups (e.g., *O*-acyl) superior to hydroxy at the β position. Treatment of β-hydroxysulfoximine **3** (R = Ph; R′ = H) with acetyl chloride/pyridine yielded only the *S*-styrylsulfoximine; reaction with *p*-toluenesulfonyl chloride in pyridine and reaction of the corresponding alkoxide in tetrahydrofuran with acetic anhydride gave unpromising mixtures. At this point we focused our work on the development of direct methods of reductive elimination of β-hydroxysulfoximines. The high reduction potential (−1.28 V)[14] of alkyl aryl sulfoximines substantially limits the choice of reducing agents.

The β-hydroxysulfoximines **4** and **5** were chosen for this



4 R = R′ = *n*-C_3H_7

5 R = *n*-C_5H_{11}, R′ = CH_3

study because the reduction products, octenes and octanols, are readily determined by gas chromatography. In addition, the resulting 2- and 4-octenes are capable of existing as isomers which would be useful for future stereochemical studies.

Pure magnesium in ethanol had no effect on the β-hydroxysulfoximine **5**. Magnesium amalgam in ethanol slowly reduced **5** to a mixture of 3-octanol (20%) and 2-octene (30%). Neither zinc nor chromium(II) perchlorate was capable of reducing the β-hydroxysulfoximine **4**. This was not unexpected since zinc and chromium(II) have oxidation potentials of less than 1 V. Sodium in liquid ammonia effected reductive cleavage of the carbon–sulfur bond of **5** to yield predominantly the alcohol. Approximately 10% of the desired alkene was formed under these conditions. Interestingly, the sodium–ammonia reduction was complete in less than 5 min. Though rapid, these conditions make this reaction unsuitable for many substances. Reduction of **5** with sodium amalgam in ethanol required 18 h to go to completion; the products were 2-octene (75%) and 2-octanol (10%).

At this point, our attention was redirected to aluminum as an agent to effect reductive cleavage. With its high oxidation potential (−1.66 V), aluminum is more than capable of reducing a sulfoximine. It has previously been reported from this laboratory that aluminum amalgam reductively cleaved β-hydroxysulfoximines to give alcohols.[13] A reinvestigation of this reaction using substrate **4** produced surprising results; treatment of **4** with aluminum amalgam in aqueous tetrahydrofuran gave 4-octene (50%) and 4-octanol (5%). This reductive elimination was not entirely satisfactory. The yield of alkene was low and the reaction required several days.

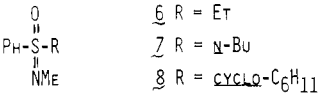
Various conditions were explored both to optimize the yield of alkene and to increase the rate. Reduction of **4** with aluminum amalgam in ethanol produced a 70% yield of 4-octene (65% *trans*-/35% *cis*-) but took 24 h to go to completion. No 4-octanol was produced under these conditions. Addition of acetic acid to the reaction mixture had a most dramatic effect. The yield of alkene was good, little alcohol was produced, and, most significantly, the reaction time was reduced to 1 h. Acetic acid was chosen because it is soluble in organic solvents but is not so strong an acid as to rapidly consume the aluminum or decompose the starting material.

Table I. Conversion of Carbonyl Compounds to Alkenes

Entry	Carbonyl compound	Sulfoximine	Yield of adduct, %	Alkene	Yield, %
1	$CH_3(CH_2)_{14}COCH_3$	**1**	90	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	90
2	$CH_3(CH_2)_{14}COCH_3$	**1**	[a]	$CH_3(CH_2)_{14}C(=CH_2)CH_3$	85
3	$CH_3(CH_2)_6CHO$	**1**	50	$CH_3(CH_2)_6CH=CH_2$	60
4	$CH_3(CH_2)_8CHO$	**1**	80	$CH_3(CH_2)_8CH=CH_2$	70
5	PhCHO	**1**	90	$PhCH=CH_2$	60
6	$CH_3(CH_2)_3CO(CH_2)_3CH_3$	**1**	90	$CH_3(CH_2)_3C(=CH_2)(CH_2)_3CH_3$	80
7		**1**	[a]		73
8		**1**	75		85
9		**1**	50		32
10		**1**	89		50
11		**1**	85		93
12	$CH_3(CH_2)_8CHO$	**6**	60	$CH_3(CH_2)_8CH=CHCH_3$[b]	60
13	$CH_3(CH_2)_4CHO$	**6**	75	$CH_3(CH_2)_4CH=CHCH_3$[c]	100
14	$CH_3(CH_2)_2CHO$	**7**	78	$CH_3(CH_2)_2CH=CH(CH_2)_2CH_3$[d]	78
15		**6**	85		65
16		**7**	75		65
17	CH_3COCH_3	**8**	TRACE		

[a] Adduct not isolated; see Experimental Section. [b] Cis/trans mixture. [c] 60% trans, 40% cis. [d] 64% trans, 36% cis. [e] 78%/22% mixture of diastereomers.

Scope of the Reductive Elimination. The scope of reductive elimination with Al(Hg)/HOAc was explored; it was found applicable to the synthesis of mono-, di-, and trisubstituted double bonds. For this work, sulfoximines **1, 6, 7,** and **8** were



6 R = Et

7 R = *n*-Bu

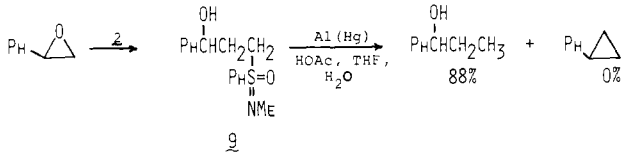
8 R = cyclo-C_6H_{11}

used. The results of these investigations are summarized in Table I. As shown, the reaction constitutes a rather general two-step procedure for the olefination of carbonyl compounds. In most cases, the hydroxysulfoximine adducts were isolated and purified prior to reduction. This is not necessary as both steps may be carried out in the same solvent and reaction vessel. When this is done, the β-hydroxysulfoximine anion is quenched with acetic acid and water and the aluminum amalgam is added. After a suitable length of time (1–4 h), the reaction mixture is worked up. Of particular interest is the high-yield methylenation of cyclic and unsaturated ketones (examples 7, 8, and 10). Cycloheptanone and cyclooctanone give low yields (less than 10%) of the exo-methylene compounds on reaction with the methylene Wittig reagent.[15] Use of the sulfoximine procedure in these cases may have distinct advantages. When sulfoximines **6** and **7** were used, the resulting alkenes were formed as mixtures of cis and trans isomers. This point is discussed in detail below.

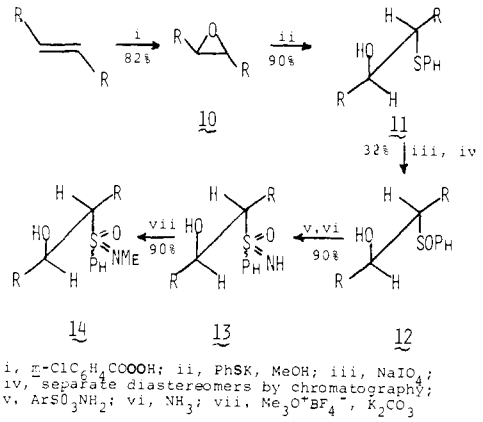
Extension of the methylenation procedure to tetrasubstituted double bonds was unsuccessful. The cyclohexylsulfoximine **8** was chosen for this work as it was felt to possess the least crowded α carbon of all the disubstituted sulfoximines. Reaction of **8** as its lithium salt with cyclohexanone led to enolization. Acetone reacted to give a very low yield of adduct which was not examined further. Lowering the temperature to −78 °C had no effect on the course of the reaction. Presumably, the steric crowding about the α carbon of the carbanion reduces its nucleophilicity to such an extent that it functions merely as a strong base.

Methylenation of aryl aldehydes is complicated by the rapid reaction of styrene derivatives with the thiophenol produced during the reductive elimination. Reduction of the β-hydrox-

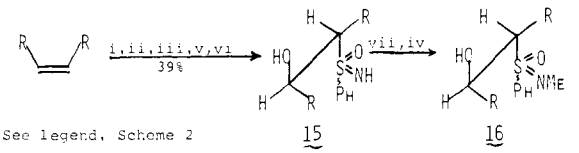
Scheme I



Scheme II. Erythro Diastereomers (R = *n*-Pr)



Scheme III. Threo Diastereomers



See legend, Scheme 2

ysulfoximine derivative **3** (R = Ph; R = H) with 16 g-atom equiv of aluminum led to the exclusive formation of 1-phenyl-2-phenylthioethane. That this arose from the reaction of styrene with the thiophenol produced during reductive cleavage was indicated by reducing *N,S*-dimethyl-*S*-phenylsulfoximine with aluminum amalgam and acetic acid in the presence of styrene; the same sulfide was again produced. The yield of aryl olefins may be increased if limited amounts (6 g-atom equiv) of aluminum are used. Even then, the yields are low and a conventional Wittig reagent would be a better choice for the olefination of an aryl aldehyde.

The reductive elimination of β-hydroxysulfoximines is analogous to the dissolving metal reduction of 1,2-dihalides to alkenes. Since 1,3-dihalides undergo a similar reduction to yield cyclopropanes,[16] the γ-hydroxysulfoximine **9** was prepared to see if 1,3 elimination was possible with sulfoximines. Reaction of styrene oxide with the lithium salt of *S*-phenyl-*N,S*-dimethylsulfoximine gave a good yield of the γ-hydroxysulfoximine **9**. This, in reduction with aluminum amalgam and acetic acid, gave only 1-phenyl-1-propanol (Scheme I). No phenylcyclopropane was detectable by gas chromatographic analysis. β-Phenylthio alcohols have been converted to cyclopropanes by an electrochemical method.[17]

Effects of Substitution on Sulfur. A study was undertaken to determine what effects substitution on sulfur had upon the reductive elimination reaction. The model system employed was the β-hydroxy sulfide (**11**). This was converted into its sulfoxides and sulfone. Each of these compounds was then subjected to the reductive elimination conditions of aluminum amalgam and acetic acid. The β-hydroxy sulfide and sulfone were inert to these conditions. The β-hydroxy sulfoxides were reduced to the sulfide but did not suffer reductive elimination.

Stereochemistry of the Reductive Elimination Reaction. As examples in Table I indicate, the olefination of aldehydes and certain ketones with α-substituted sulfoximines proceeds to give mixtures of cis and trans alkenes. Our objective in this portion of the work was to study the origin of these cis/trans mixtures.

Table II. Reduction of Pure Diastereomers

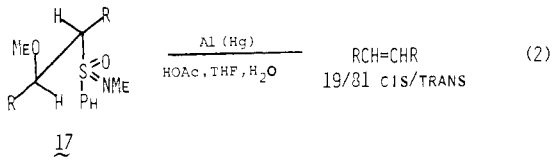
diastereomer	4-octene cis/trans	diastereomer	4-octene cis/trans
14a	40/60	**16b**	23/77
14b	30/70	mixture[a]	36/64
16a	16/84		

[a] From addition of **4** to butanal.

The model systems for this study were the β-hydroxysulfoximines **4** derived from *S*-butyl-*N*-methyl-*S*-phenylsulfoximine (**7**) and butanal. These derivatives possess three chiral centers which allow for the existence of four *dl* pairs. The reaction of the sulfoximine **7** with butanal proceeds to yield a mixture of all four possible diastereomeric β-hydroxysulfoximines as evidenced by the presence of four distinct *N*-methyl singlets in the ^{1}H NMR of the crude adduct.

The independent syntheses of the individual diastereomers are illustrated in Schemes II and III. Upon reduction each diastereomer gave rise to a mixture of *cis*- and *trans*-4-octenes. The cis to trans ratios varied somewhat but not significantly (Table II).

The β-hydroxysulfoximines exhibit a strong intramolecular hydrogen bond in the infrared. The question arose as to whether or not intramolecular hydrogen bonding had any effect on the cis–trans composition of the alkenes produced by reductive elimination. To study this, a series of OH and NH substituted β-hydroxysulfoximines was prepared. The derivatives had various arrangements of OH, NH, O-Me, and N-Me substitution. Each of the β-hydroxysulfoximine derivatives was reductively eliminated as before; there was little variation in the cis to trans ratios (e.g., eq 2), leading to the



(2)

conclusion that intramolecular hydrogen bonding has little effect on the ratio of cis to trans olefins produced by the reductive elimination of β-hydroxysulfoximines.

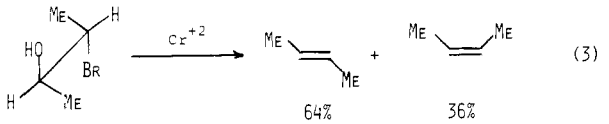
The possibility remained that some other process was responsible for the cis–trans mixtures. One possibility was that the diastereomeric β-hydroxysulfoximines were being interconverted under the reaction conditions. To test this, the pure diastereomer **14a** was treated with acetic acid, tetrahydrofuran, and water for 6 h. On workup, **14a** was recovered unchanged. As a further test, **14a** was reduced with aluminum amalgam and the reaction stopped at 65% completion. Isolation of the unreacted β-hydroxysulfoximine showed that it was again unchanged.

The β-hydroxysulfoximines are cleaved in poor yield to alcohols by aluminum amalgam. It was thought that perhaps the olefin was being formed by first a reductive cleavage to an alcohol which then underwent elimination to alkenes. This process would explain the cis–trans mixtures but would also be expected to yield positional isomers. To test this possibility, 4-octanol was treated with aluminum amalgam and acetic acid. No alkene was formed under these conditions.

A further possibility is that each diastereomeric β-hydroxysulfoximine gives rise to a pure cis or trans alkene, but the reaction conditions cause isomerization. To test this, pure *cis*- and *trans*-4-octene were treated with aluminum amalgam and acetic acid. The trans isomer was recovered unchanged. The *cis*-4-octene isomerized to the extent of 8%. This change is too small to account for the cis–trans ratios obtained by reductively eliminating the β-hydroxysulfoximines.

Finally, it is possible that an intermediate formed during the reduction of a β-hydroxysulfoximine caused an interconversion of the cis and trans alkenes. To test this, β-hydroxysulfoximine **3** (R = *n*-$C_{15}H_{31}$; R′ = CH_3) was reductively eliminated in the presence of a known mixture of *cis*- and *trans*-4-octene. After reduction was complete, the 4-octenes were isolated and analyzed for cis and trans content. A 10% conversion of the *cis*-4-octene to *trans*-4-octene was observed. This is what was expected based on the previous experiments.

The β-hydroxysulfoximines are analogous to halohydrins. Halohydrins undergo reductive elimination with various reducing agents to yield alkenes.[18] Erythro and threo halohydrins yield mixtures of cis and trans alkenes on reduction (eq 3). The



(3)

chromium(II) reduction of 3-bromo-2-butanol has been studied in detail.[19] It was found that the pure erythro and threo diastereomers gave similar mixtures of *cis*- and *trans*-2-butenes on reduction. To account for this, a mechanism was proposed which involves an initial reduction to give a radical. This undergoes further reduction to yield a carbanion or organometallic species which then eliminates to alkene. Inversion of the radical or organometallic species prior to elimination results in the mixtures of cis and trans alkenes.

A similar mechanism can be written for the reductive elimination of β-hydroxysulfoximines. The radical intermediate can react in several ways. It can abstract a hydrogen atom from the solvent to give alcohols or it can invert and lose a hydroxyl radical to give mixtures of cis and trans alkenes. Loss of a hydroxyl radical is unlikely for energetic reasons. Attempts to trap the radical intermediate with butyl mercaptan failed. This does not entirely rule out a radical intermediate since it may be tightly associated with an aluminum atom. A more reasonable mechanism involves the further reduction of the radical to a carbanion or organoaluminum compound.

The mechanism most consistent with the experimental results is one involving the reductive cleavage of the carbon–sulfur bond to give a carbanion or organoaluminum compound. This mechanism involves the transfer of two electrons from aluminum metal to the sulfoximine to give a tetracoordinate sulfur intermediate **18** (Scheme IV). Collapse of **18** yields a carbanion or organoaluminum compound and a sulfinamide. Further reduction of the sulfinamide yields thiophenol, the observed sulfur-containing product. The intermediate may undergo protonation to yield alcohols or inversion and elimination to yield observed mixtures of cis and trans alkene. The ratio of alkene to alcohol depends on what metal is used as the reducing agent. As shown in Table III the ratio of alkene to alcohol increases as the Lewis acidity of ions from reducing agent increases.

This mechanism requires as the first step the reduction of the sulfoximine. Alkyl aryl sulfoximines have a reduction potential of −1.28 V and, therefore, only those reducing agents whose oxidation potentials are greater than this should be effective in reductively eliminating β-hydroxysulfoximines.

Scheme IV

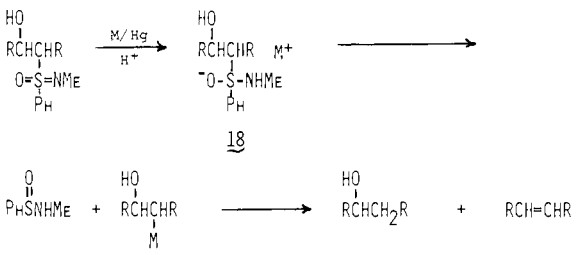


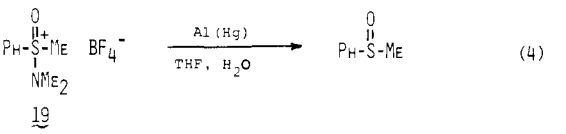
Table III. Effect of Reducing Agent on Ratio of Alkene to Alcohol

$$\mathbf{5} \xrightarrow{M/Hg} \text{2-octene} + \text{3-octanol}$$

	reducing agent	% 2-octene	% 3-octanol
increasing Lewis acidity of metal ions ↓	Na/Hg EtOH	10	90
	Mg/Hg EtOH	70	30
	Al/Hg EtOH	100	0

Sodium, magnesium, and aluminum were all capable of reductively eliminating β-hydroxysulfoximines. These metals have oxidation potentials of 2.95, 2.44, and 1.66 V, respectively. Zinc and chromium(II) have oxidation potentials of less than 1 V and hence they were ineffective at reducing sulfoximines.

The rate enhancement of acetic acid is consistent with this mechanism. One possible role of the acid is to protonate the sulfoximine nitrogen and lower its reduction potential. This would result in an increased rate of reduction. This effect may be ruled out for two reasons. First, the reduction potential of alkyl aryl sulfoximines is insensitive to changes in pH over the range of pH 2.1–8.5. Second, reduction of a protonated sulfoximine would be expected to yield the same products as reduction of the *N,N*-dimethylsulfoximine salt **19**[13] (eq 4). The



(4)

acetic acid could also function by protonating the hydroxyl group. This would generate a better leaving group, lower the activation energy of the elimination, and increase the rate. The aluminum amalgam reduction without acetic acid produces voluminous aluminum salts which coat the metal and hinder mixing of the reactants. With acetic acid added, the reaction produces a thin slurry and the metal remains relatively clean. The sodium reductions are very fast and there is no accumulation of insoluble material. Thus, the role of the acetic acid may well be to dissolve the aluminum salts and keep the metal surface clean. The aluminum acetate may also be involved as a Lewis acid in facilitating the loss of the hydroxyl group (see Table III).

Experimental Section

General Procedure for Preparation of Sulfoximine Adducts. The sulfoximine (0.01 mol) was dissolved in dry tetrahydrofuran (25 mL), triphenylmethane (15 mg) was added, and the solution was cooled to 0 °C under nitrogen with stirring. A solution of butyllithium (1.5 M in hexane) was added until an orange color persisted. The carbonyl compound (0.01 mol) in dry tetrahydrofuran (15 mL) was added over 5 min and the mixture stirred for 0.5 h at 0 °C (for conjugated carbonyl compounds, the reaction mixture was worked up at this point) and then for 1 h at room temperature. Then the mixture was poured into 10% aqueous ammonium chloride (150 mL) and extracted twice with 25-mL portions of dichloromethane. The extracts were washed with water (50 mL), dried ($MgSO_4$), and evaporated. The crude β-hydroxysulfoximines were purified by crystallization or column chromatography over silica gel.

General Procedure for Reductive Elimination of β-Hydroxysulfoximines. The β-hydroxysulfoximine (0.01 mol) was dissolved in tetrahydrofuran (75 mL), and acetic acid (35 mL) and water (35 mL) were then added. Granular aluminum (60 mesh, 0.16 g-atom), which had been stirred for 2 min with 2% aqueous mercuric chloride (100 mL), filtered, and washed successively with water and ethanol, was added to the reaction mixture. Stirring was continued until TLC showed no starting material (1–4 h). The mixture was filtered through Celite and washed with tetrahydrofuran. The filtrate was diluted with water (300 mL) and extracted twice with 300-mL portions of pentane. The pentane extracts were washed twice with 20% aqueous sodium

hydroxide (100 mL) and once with water (100 mL) and dried ($MgSO_4$). The pentane was removed by distillation or evaporation and the crude alkene was purified by distillation or column chromatography.

Methylenation of Carbonyl Compounds without Isolation of the Adduct. The sulfoximine (0.01 mol) was dissolved in dry tetrahydrofuran (25 mL), triphenylmethane (15 mg) was added, and the solution was stirred at 0 °C under nitrogen. A solution of butyllithium (1.5 M in hexane) was added until an orange color persisted. The carbonyl compound (0.01 mol) in dry tetrahydrofuran (15 mL) was added over 5 min and the mixture stirred for 0.5 h at 0 °C and 1 h at room temperature. Acetic acid (35 mL) was added followed by tetrahydrofuran (35 mL) and water (35 mL). Aluminum amalgam (0.16 g-atom) prepared as above was added and the reaction was carried out as above.

***erythro*-5-Phenylthio-4-octanol.** Potassium metal (6.0 g, 0.15 g-atom) was dissolved in 200 mL of methanol and thiophenol (16.5 g, 0.15 mol) was added. A solution of *trans*-4-octene oxide (**10**), bp 110–112 °C (140 mm) (12.8 g, 0.10 mol), in 15 mL of methanol was added and the mixture stirred at room temperature for 2 h and then refluxed for 8 h. The mixture was cooled, poured into 500 mL of water, and extracted three times with 100-mL portions of dichloromethane. The combined dichloromethane extracts were washed with 100 mL of 10% aqueous sodium hydroxide and 100 mL of water and dried over magnesium sulfate. The drying agent was filtered off and the filtrate evaporated to yield 21.4 g (90%) of **11** as a colorless oil.

***erythro*-(2-Hydroxy-1-propylpentyl) Phenyl Sulfoxides (12a,b).** The hydroxy sulfide **11** (23.8 g, 0.10 mol) was dissolved in 300 mL of methanol and 300 mL of water was added. The mixture was cooled to 0 °C with stirring and 22.7 g (0.105 mol) of powdered sodium metaperiodate was added. The mixture was stirred at 0–5 °C for 6 h and then for 12 h at room temperature. The mixture was poured into 2 L of water and extracted three times with 200-mL portions of chloroform. The combined chloroform extracts were washed with 200 mL of water and dried over magnesium sulfate. The drying agent was filtered off and the filtrate evaporated to yield a crystalline solid. This was dissolved in boiling ether and cooled to room temperature. The crystals (6.0 g) of pure **12a,** mp 96–98 °C, were collected. The filtrate was evaporated and the residue was chromatographed over 400 g of silica gel using a 60:40 mixture of ether and pentane. Evaporation of the fractions yielded 9.0 g (32%) of **12b,** mp 70–72 °C, and 2.0 g of **12a.** The total yield of **12a** was 8.0 g (32%).

***erythro*-5-Phenylsulfonimidoyl-4-octanol (13a).** The β-hydroxy sulfoxide **12a** (4.5 g, 0.018 mol) was dissolved in 60 mL of dichloromethane and cooled to 0 °C with stirring. A solution of mesitylsulfonyloxyamine (5.8 g, 0.027 mol) in 40 mL of dichloromethane was added and the mixture stirred for 0.5 h at 0 °C and then for 2 h at room temperature. The mixture was poured into a cold solution of concentrated ammonium hydroxide (100 mL) and water (200 mL). The dichloromethane layer was separated and the aqueous layer extracted three times with 100-mL portions of chloroform. The combined dichloromethane and chloroform extracts were washed with 100 mL of 10% aqueous ammonium chloride and 100 mL of water and dried over magnesium sulfate. The drying agent was filtered off and the filtrate evaporated to yield a viscous oil. The oil was dissolved in 75 mL of chloroform and extracted three times with 10% sulfuric acid. The combined acid extracts were washed with 100 mL of chloroform and then were made basic with concentrated ammonium hydroxide. The basic solution was extracted with three 100-mL portions of chloroform. The combined chloroform extracts were washed with 100 mL of 10% aqueous ammonium chloride and 100 mL of water and dried over magnesium sulfate. The drying agent was removed and the solution evaporated to yield 2.1 g (78%) of **13b** as a colorless oil.

***erythro*-5-(*N*-Methylphenylsulfonimidoyl)-4-octanol (14a).** The β-hydroxysulfoximine **13a** (3.5 g, 0.013 mol) was dissolved in 30 mL of dichloromethane and cooled to 0 °C with stirring. Anhydrous potassium carbonate (2.2 g, 0.016 mol) and trimethyloxonium fluoroborate (2.2 g, 0.015 mol) were added and the mixture was stirred for 0.5 h at 0 °C and then for 2 h at room temperature. The mixture was poured into 200 mL of 10% aqueous ammonium chloride and the dichloromethane layer was separated. This was washed with 50 mL of water, dried over magnesium sulfate, filtered, and evaporated to yield a viscous oil. The oil was chromatographed over 250 g of silica gel using a 1:1 ether–pentane mixture. Evaporation of the fractions gave 3.4 g (90%) of **14a** as a colorless oil.

***erythro*-5-(*N*-methylphenylsulfonimidoyl)-4-octanol (14b)** was prepared as a colorless oil in 87% yield from the β-hydroxysulfoximine **13b** by the procedure used for **14a.**

***threo*-5-Phenylthio-4-octanol** was prepared as a colorless oil in 95% yield from *cis*-4-octene oxide, bp 99–100 °C (105 mm), by the procedure used for **11.**

***threo*-5-Phenylsulfinyl-4-octanols** were prepared from the above β-hydroxy sulfide as a colorless oil in 95% yield. The oxidation was carried out by the procedure used for **12a** and **12b;** the diastereomeric β-hydroxy sulfoxides were not separated.

***threo*-5-(Phenylsulfonimidoyl)-4-octanols (16a,b).** The mixture of diastereomeric β-hydroxysulfoximines **15** was methylated by the procedure used for **14a.** The diastereomeric *N*-methyl-β-hydroxysulfoximines were separated by column chromatography over silica gel to yield **16a** (18.5%) and **16b** (31%). Recrystallization of **16b** from pentane gave white crystals, mp 48–50 °C.

***erythro*-4-Methoxy-5-phenylthiooctane.** The β-hydroxy sulfide **11** (11.9 g, 0.05 mol) was dissolved in 50 mL of dry tetrahydrofuran. Triphenylmethane (15 mg) was added and the solution cooled to 0 °C under nitrogen with stirring. A solution of butyllithium (1.5 M in hexane) was added until an orange color persisted. To this was added 150 mL of dry *N,N*-dimethylformamide. Methyl iodide (14.2 g, 0.10 mol) in 50 mL of dry *N,N*-dimethylformamide was added over 5 min and the mixture stirred for 1.5 h at room temperature. The mixture was poured into 1 L of 5% aqueous ammonium chloride and extracted twice with 300-mL portions of ether. The combined ether extracts were washed with 200 mL of 10% aqueous sodium thiosulfate and 200 mL of water and dried over magnesium sulfate. The drying agent was filtered off and the filtrate evaporated to yield a colorless oil. This was chromatographed over 250 g of silica gel using a 1:19 ether–pentane mixture to yield 12.0 g (90%) of product as a colorless oil.

***erythro*-2-(Methoxy-1-propylpentyl) Phenyl Sulfoxides.** The above sulfide was oxidized by the procedure used for **12a** and **12b** to yield a mixture of diastereomeric β-methoxy sulfoxides. These were separable by column chromatography on silica gel into A (25%) and B (30%) as colorless oils.

***erythro*-*S*-(2-Methoxy-1-propylpentyl)-*S*-phenylsulfoximine.** The β-methoxy sulfoxides (A and B, above) were aminated by the procedure used for **13a** to yield the products C (74%) and D (85%), respectively, as colorless oils.

***erythro*-*S*-(2-Methoxy-1-propylpentyl)-*N*-methyl-*S*-phenylsulfoximine (17).** The β-methoxysulfoximines C and D were methylated by the procedure used for **14a** to yield **17a** and **17b** as colorless oils in 80 and 84% yield, respectively.

***erythro*-5-Phenylsulfonyl-4-octanol.** *m*-Chloroperbenzoic acid (Aldrich, 85%, 2.07 g, 0.012 mol) was dissolved in 40 mL of dichloromethane and cooled to 0 °C with stirring. The β-hydroxy sulfide **11** (1.19 g, 5 mmol) in 5 mL of dichloromethane was added in one portion and the mixture was stirred for 2 h at 0 °C and then for 3 h at room temperature. The *m*-chlorobenzoic acid was filtered off and the filtrate was washed twice with 25-mL portions of 10% aqueous sodium hydrogen carbonate and 25 mL of water. The dichloromethane layer was dried over magnesium sulfate, filtered, and evaporated to yield a colorless oil. This was chromatographed over 60 g of silica gel using a 3:7 ether–pentane mixture to yield 1.05 g (78%) of sulfone as a colorless oil.

3-(*N*-Methylphenylsulfonimidoyl)-1-phenyl-1-propanol (9). *N,S*-Dimethyl-*S*-phenylsulfoximine (1.69 g, 0.01 mol) was dissolved in 20 mL of dry tetrahydrofuran. Triphenylmethane (15 mg) was added and the solution cooled to 0 °C under nitrogen with stirring. A solution of butyllithium (1.5 M in hexane) was added dropwise until an orange color persisted. Styrene oxide (1.20 g, 0.01 mol) in 10 mL of dry tetrahydrofuran was then added in one portion. The mixture was stirred for 2 h at 0 °C and then for 12 h at room temperature. The mixture was poured into 100 mL of 10% aqueous ammonium chloride and extracted twice with 50-mL portions of dichloromethane. The combined dichloromethane extracts were washed with water (50 mL), dried over magnesium sulfate, filtered, and evaporated to yield a yellow solid. This was recrystallized three times from benzene to yield 1.5 g (52%) of **9** as white needles, mp 111–115 °C (mixture of diastereomers).

***S*-Ethyl-*N*-methyl-*S*-phenylsulfoximine (6).[20]** *S*-Ethyl-*S*-phenylsulfoximine was prepared as an oil in 80% yield by reaction of ethyl phenyl sulfoxide with hydrazoic acid. This sulfoximine (16 g) was treated with 20 mL of 40% formaldehyde and 180 mL of 90% formic acid for 4 days on a steam bath to yield 30 g (85%) of an oil.

***S*-Butyl-*N*-methyl-*S*-phenylsulfoximine (7).[20]** *S*-Butyl-*N*-

methyl-*S*-phenylsulfoximine was obtained as an oil. Butyl phenyl sulfide, bp 125–130 °C (3 mm), was oxidized to the sulfoxide with hydrogen peroxide. The sulfoxide was converted to the oily sulfoximine by hydrazoic acid. The sulfoximine was methylated using formaldehyde and formic acid using the procedure described above.

S-Cyclohexyl-*N*-methyl-*S*-phenylsulfoximine (8).[20] Cyclohexyl phenyl sulfide, bp 117–120 °C (1.5 mm), was prepared in 50% yield by the reaction of sodium thiophenoxide with bromocyclohexane. Periodate oxidation of the sulfide gave cyclohexyl phenyl sulfoxide, mp 63–65 °C, in 89% yield. Reaction of the sulfoxide with mesitylsulfonyloxyamine gave *S*-cyclohexyl-*S*-phenylsulfoximine, mp 74–75 °C, in 65% yield. The sulfoximine was methylated with trimethyloxonium fluoroborate in the presence of sodium carbonate to give **8** in 80% yield as a viscous oil.

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Supplementary Material Available: Analytical and spectral data (8 pages). Ordering information is given on any current masthead page.

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Excited-State Chemistry of 1-Alkenyl-2-pyridones. Exploratory and Mechanistic Investigations and Kinetic Analysis of Photocyclization Reactions Involving Conversion of the *N*-Vinylamide to Oxazolium Ylide Function[1]

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Abstract: The excited-state chemistry of 1-alkenyl-2-pyridones has been subjected to detailed study. The isobutenyl- (**1**) and propenyl- (**2**) 2-pyridones undergo the familiar Dewar-pyridone forming electrocyclization and $_{\pi}4 + _{\pi}4$ dimerization when irradiated in solvents of low polarity. The nature of pathways followed by these systems changes when reactions are conducted in polar solvents such as methanol and water. Under these conditions electrocyclization of the *N*-vinylamide occurs to generate eventually the pyridonylethanol derivatives **7** and **8** from singlet excited alkenylpyridones. Irradiations of aqueous solutions of **1** and **2** containing perchloric acid lead to production of the oxazolo[3,2-*a*]pyridinium perchlorates (**9** and **10**). Information has been accumulated to support mechanisms for these processes involving initial generation of azomethine ylides **28**, which are trapped by water or hydronium ion to give oxazolopyridinium salts. The hydroxide salts produced by proton transfer from water are then transformed under mild workup conditions to the corresponding pyridonylethanols. Detailed kinetic analysis of the singlet reaction and decay pathways for the isobutenyl-2-pyridone has been performed using a variety of photochemical and photophysical techniques. This has yielded individual rate constants for singlet-pyridone conversion to Dewar pyridone and pyridinium ylide, singlet decay and emission, and ylide trapping by water and return to ground-state pyridone. The interesting solvent polarity dependence of the nature of photochemical reaction pathways followed by the 1-alkenyl-2-pyridones has been explored using measured singlet lifetimes, fluorescence efficiencies, and reaction quantum yields and interpreted in terms of a dramatic effect of solvent polarity on rate constants for conversion of singlet 1-alkenyl-2-pyridones to the dipolar, azomethine ylides. Solvent polarity effects on singlet lifetimes of a number of systems containing *N*-vinylamide and related divinylamine chromophores have been noted. Lastly, the effect of alkyl substitution on 1-alkenyl-2-pyridone cyclization efficiency is discussed in terms of ground and singlet excited state conformational control.

Photochemical investigations of systems containing more than one potentially reactive chromophore have uncovered a wealth of information about the physical and chemical characteristics of excited states of organic substances. As a result, organic materials containing numbers of different photochemically reactive groupings continue to serve as appealing targets for ongoing explorations. An analysis of one such system, the 1-alkenyl-2-pyridones (1), reveals the potential for diverse types of photochemical behavior due to the presence of the pyridone,[3] 1-vinylamide,[4] oxadi-π-amine,[5] and di-π-amine[6,7] chromophores. Indeed, the excited-state chemistry of systems containing each of these moieties either has been

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