1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.3 (m, 5, Ph), 5.8 (br s, 1, OH), 4.8–2.8 (m, 3, SCH_2CHO), 2.7 (s) 2.6 (s; 3, NCH_3 for both diastereomers), 2.2–0.6 (m, 9, *i*-Bu). Anal. ($C_{13}H_{21}NO_2S$) C, H, N.

(*SS*,2*S*)- and (*SS*,2*R*)-3,3-Dimethyl-1-1-(*N*-methylphenylsulfonimidoyl)-2-butanol were obtained (65%) as a mixture (ca. 2.8:1 by integration of the areas for the *tert*-butyl protons of the two structures) from the reaction of (+)-1 with 2,2-dimethylpropanal. The mixture was a pale yellow oil at room temperature and displayed the following spectral characteristics: IR (neat) 3300 (br), 1250 (br), 1150 cm^{-1} (sh at 1100 and 1080); ^1H NMR ($CDCl_3$) δ 8.1–7.4 (m, 5, Ph), 5.7 (br s, 1, OH), 4.2–2.8 (m, 3, SCH_2CHO), 2.7 (s), 2.6 (s; 3, NCH_3 signals for the diastereomers), 0.9 (s), 0.8 (s; 9, $C(CH_3)_3$ signals of the diastereomers).

Hydrogenolysis of β-Hydroxy Sulfoximines with Raney Nickel W-2. The β-hydroxy sulfoximine was added to a two-neck flask fitted with a mechanical stirrer and dissolved in a minimal amount of water-saturated diethyl ether. **(Caution**: Failure to use water-saturated ether can result in fires.) Twenty equivalents of Raney nickel W-2 (measured as per directions in "Organic Syntheses")[10] were transferred to the sulfoximine soluton. The reaction mixture was vigorously stirred at room temperature and the progress of the reaction was monitored by TLC. When no starting material remained, stirring was stopped and the solvent was carefully decanted. The residue was washed twice by suspension, and the organic layers were combined. The combined organic layers were dried ($MgSO_4$), filtered through Celite, and concentrated by distillation. The product alcohol was obtained from the residue in high purity by short-path distillation or chromatography.

(10) Mozingo, R., "Organic Syntheses", Collect. Vol. 3; Wiley: New York, 1955; p 181.

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Registry No. (+)-(*S*)-1, 33993-53-2; (−)-(*R*)-1, 80482-67-3; (*S*,*S*,2*S*)-2 (R = Ph; R′ = Me), 80441-25-4; (*SS*,2*R*)-2 (R = Ph; R′ = Me), 80441-26-5; (*SS*,2*S*)-2 (R = Ph; R′ = Et), 73798-17-1; (*SS*,2*R*)-2 (R = Ph; R′ = Et), 73798-18-2; (*SS*,2*S*)-2 (R = Ph; R′ = Pr), 80441-27-6; (*SS*,2*R*)-2 (R = Ph; R′ = Pr), 80441-28-7; (*SS*,2*S*)-2 (R = Ph; R′ = Bu), 80441-29-8; (*SS*,2*R*)-2 (R = Ph; R′ = Bu), 80441-30-1; (*SS*,1*S*)-2 (R = Ph; R′ = cyclohexyl), 80441-31-2; (*SS*,1*R*)-2 (R = Ph; R′ = cyclohexyl), 80441-32-3; (*SS*,2*S*)-2 (R = CH_2Ph; R′ = Et), 80441-33-4; (*SS*,2*R*)-2 (R = CH_2Ph; R′ = Et), 80441-34-5; (*SR*,3*S*)-2 (R = Et; R′ = Bu-*i*), 80441-35-6; (*SR*,3*R*)-2 (R = Et; R′ = Bu-*i*), 80441-36-7; (*SS*,1*S*)-2 (R = H; R′ = Ph), 33903-51-4; (*SS*,1*R*)-2 (R = H; R′ = Ph), 72174-41-5; (*SS*,2*S*)-2 (R = H; R′ = hexyl), 80422-48-6; (*SS*,2*R*)-2 (R = H; R′ = hexyl), 80422-49-7; (*SS*,2*S*)-2 (R = H; R′ = Bu-*i*), 80422-50-0; (*SS*,2*R*)-2 (R = H; R′ = Bu-*i*), 80422-51-1; (*SS*,2*S*)-2 (R = H; R′ = Bu-*t*), 78742-30-0; (*SS*,2*R*)-2 (R = H; R′ = Bu-*t*), 78742-34-4; (+)-3 (R = Ph; R′ = Et), 1006-06-0; (−)-3 (R = Phf R′ = Et), 53777-08-5; (+)-3 (R = Ph; R′ = Pr), 52992-90-2; (−)-3 (R = Ph; R′ = Pr), 52992-91-3; (+)-3 (R = Ph; R′ = Bu), 73464-88-7; (−)-3 (R = Ph; R′ = Bu), 19641-54-4; (+)-3 (R = Ph; R′ = hexyl), 80441-37-8; (−)-3 (R = Ph; R′ = hexyl), 80441-38-9; (+)-3 (R = CH_2Ph; R′ = Et), 56640-51-8; (−)-3 (R = CH_2Ph; R′ = Et), 55016-95-0; (+)-3 (R = Bu-*i*; R′ = Et), 80513-04-8; (−)-3 (R = Bu-*i*; R′ = Et), 19113-77-0; (±)-3 (R = H; R′ = Ph), 13323-81-4; (±)-3 (R = H; R′ = hexyl), 4128-31-8; (±)-3 (R = H; R′ = Bu-*i*), 20281-88-3; (±)-3 (R = H; R′ = Bu-*t*), 20281-91-8; acetophenone, 98-86-2; 1-phenyl-1-propanone, 93-55-0; 1-phenyl-1-butanone, 495-40-9; 1-phenyl-1-pentanone, 1009-14-9; cyclohexyl phenyl ketone, 712-50-5; 1-phenyl-2-butanone, 1007-32-5; 5-methyl-3-hexanone, 623-56-3; benzaldehyde, 100-52-7; heptanal, 111-71-7; 3-methylbutanal, 590-86-3; 2,2-dimethylpropanal, 630-19-3.

Diastereoselective Reductions of β-Keto Sulfoximines

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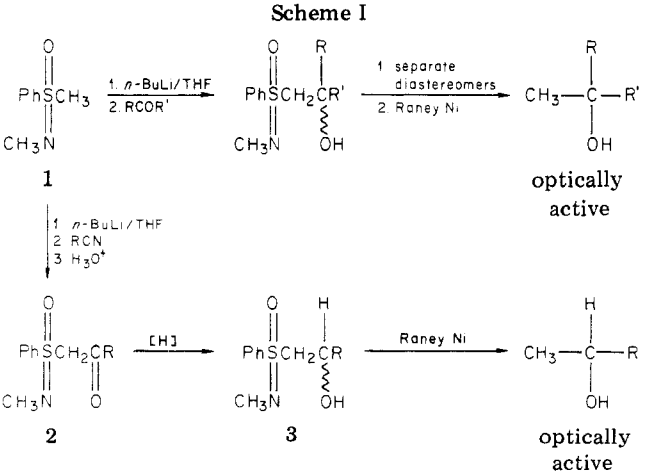
(*S*)-β-Keto sulfoximines have been prepared by butyllithium-mediated condensation of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine with nitriles. The β-keto sulfoximines on treatment with a variety of reducing agents afforded β-hydroxy sulfoximines with varying diastereomeric ratios. Highest asymmetric inductions were observed with gaseous diborane. A sulfoximine–borane complex is suggested as an intermediate. Raney nickel desulfurization of the β-hydroxy sulfoximines afforded secondary alcohols with optical purities in the 18–69% range.

The addition of optically active *N*,*S*-dimethyl-*S*-phenylsulfoximines (1) to prochiral ketones followed by chromatographic separation of the diastereomeric adducts and desulfurization has been shown to be a viable route to optically active tertiary alcohols (Scheme I).[1] A similar scheme applied to aldehydes and resulting in optically active secondary alcohols was less successful due to difficulties in chromatographic resolution of the adducts.[1,2] Diastereoselective reduction of β-keto sulfoximines derived from 1 was envisioned as an alternate approach to requisite β-hydroxy sulfoximines (Scheme I). It was anticipated that steric and/or chelation control would lead to significant asymmetric induction at the carbinol site.

Since the completion of this work, a similar study has appeared by Cinquini and co-workers.[3] They prepared keto sulfoximines 2 in 49–69% yields by condensation of the lithium reagent derived from (+)-(*S*)-1 with esters and examined reduction of these substances with sodium bo-

Scheme I



(1) Johnson, C. R.; Stark, C. J., Jr. *J. Org. Chem.*, preceding paper in this issue.
(2) Schroeck, C. W.; Johnson, C. R. *J. Am. Chem. Soc.* **1971**, *93*, 5305.
(3) Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1109.

0022-3263/82/1947-1196$01.25/0

Table I. β-Keto Sulfoximines by Condensation of (+)-(S)-1 with Nitriles

compd	keto sulfoximine, R	% yield	mp, °C
2a	Ph	79	90–93
2b	*t*-Bu	69	oil
2c	$(CH_2)_5CH_3$	80	35–37
2d	*i*-Bu	63	oil

rohydride (asymmetric induction: 0–50%).

Results and Discussion

β-Keto sulfoximines were prepared by the butyllithium mediated addition of 1 to nitriles (Scheme I and Table I). All of the β-keto sulfoximines exhibit a characteristic IR band near 1600 cm^{-1} and a ^1H NMR peak near δ 4.5 due to significant enol content.

Optically active β-keto sulfoximines (**2a** and **2b**) were treated with a number of achiral reducing agents (Table II). Bulky nucleophilic reducing species were the first reagents utilized, in attempts to produce the significant steric interactions between the chiral substrate and reagent requisite for a high degree of asymmetric induction. It became quickly apparent that many of these reagents were too basic to be utilized with the highly enolic keto sulfoximines. Attempted reductions with $LiAlH(O\text{-}t\text{-}Bu)_3$, $NaHB(O\text{-}i\text{-}Pr)_3$, and K-Selectride resulted in essentially total recovery of starting material (entries 1–3, Table II). For example, addition of K-Selectride to a THF solution of **2a** resulted in an immediate and vigorous evolution of gas and eventual recovery of greater than 85% of the starting material. Attempted reductions with $LiAlH_4$ were also accompanied by gas evolution, indicative of the reaction of an acidic proton of the substrate with the hydride.[4] Addition of a THF solution of **2b** to a solution of 3 equiv of $LiAlH_4$ in THF resulted in little reduction after 2 h, as determined by thin-layer chromatography. Refluxing the mixture for 90 min failed to induce reaction and upon workup a mixture of 87% starting material and 13% product, reflecting an 86% material balance, was isolated. The ratio of diastereomers, determined by NMR, was approximately 2:1. When **2b** was treated with a standardized solution of $LiAlH_4$, in diethyl ether at −23 °C (a temperature that prevented decomposition of the β-keto sulfoximine to an undetermined material), 30% reduction was achieved on the basis of 90% material balance. The product epimers were formed in a 70:30 ratio.

Accordingly, attention was turned to less basic nucleophilic species (entries 6–8, Table II). Although the yields of the desired product were high, the diastereomeric ratios were nearly unity. The yields realized with these reagents substantiates the belief that more basic reagents served only to effect enolate formation of the substance.

Next, attempts were made to reduce the β-keto sulfoximines with electrophilic species. Treatment of **2a** with disiamylborane in THF resulted, under typical experimental conditions, in the recovery of starting material in low material balance; the reaction was not investigated further. When, however, **2b** was treated with BH_3·THF at −78 °C, a 90% reduction was achieved, producing nearly a 4:1 diastereomeric ratio (based on a 91% material balance). Such a high degree of 1,3-asymmetric induction may be attributable to intramolecular delivery of the hydride by BH_3 coordinated to the basic sulfoximine nitrogen. The borane–sulfoximine complex has analogy in borane–amine complexes which are well-known reducing agents.[5] Studies by Brienne, Tramontini, Angiolini, and others have shown that various asymmetric additions to prochiral carbonyl compounds are influenced by a β-amino group in the substrate; results have been rationalized on the basis of a cyclic model.[6]

It was suspected that competition between the THF and substrate for coordination of the borane might have existed, leading to reduction via different paths and resulting in reduced optical yields. It seemed reasonable that use of a less polar solvent might increase the proportion of the reaction that proceeded via a mechanism involving coordination of "BH_3" to the substrate.

With this in mind, a solution of (*SS*)-2-(*N*-methylphenylsulfonimidoyl)-1-phenylethanone, **2a**, in benzene was stirred in an inert atmosphere and 1.5 equiv of gaseous diborane was bubbled through the solution. After the reaction mixture was stirred for 2 h, aqueous 2 N hydrochloric acid was added to quench the reaction. ^1H NMR of the reaction products indicated only a trace of the desired product, but it occurred almost exclusively as one diastereomer. The bulk of the material was unidentifiable. No trace of starting material could be found, and the infrared data indicated the absence of a carbonyl or an alcohol. The reaction was reinvestigated and an interesting decomposition was deduced. Treatment of the β-keto sulfoximine with diborane in benzene, followed by addition of aqueous sodium hydroxide and 30% hydrogen peroxide, resulted in a combined 64% yield of 2-phenylethanol and 1-phenylethanol in an 84:16 ratio. Apparently under these reaction conditions **2a** decomposed to styrene, which was then hydroborated by excess diborane. Such a proposal was at odds with the well-known generalization that hydroboration does not proceed in the absence of an ethereal solvent.[7] Nonetheless, it was demonstrated that a solution of styrene in benzene, when treated with diborane in a fashion analogous to the previous reaction, resulted in an 85% yield of the same 84:16 ratio of isomers.

It was observed that lowering the reaction temperature resulted in good yields of the desired β-hydroxy sulfoximines with exceedingly good diastereomeric ratios. In these experiments, toluene (lower freezing) rather than benzene was used as solvent. In this way, the diastereomeric ratios shown in Table III were observed. For more precise determination of the diastereomeric ratios, hydrogenolysis to the corresponding alcohol was effected. In order for the percent optical purity to be accurate reflection of the diastereomeric ratio, we avoided procedures that might have resulted in diastereomeric enrichment. In some of the reductions conducted at −23 °C, a trace of starting keto sulfoximine was isolated with the product, but control experiments indicated that the keto sulfoximines produced no alcohol upon reaction with Raney nickel. Therefore, their presence in the hydrogenolysis step would not be deleterious. The results of the hydrogenolysis step are displayed in Table IV; the optical yields obtained agree favorably with the values discerned from the ^1H NMR spectra of the β-hydroxy sulfoximines. The optical yields of the aliphatic alcohols are among the highest obtained by any asymmetric synthesis. In every case studied, β-keto sulfoximines of the *S* configuration gave rise to secondary alcohols with the *S* configuration.

In order to gain mechanistic insight into these reductions, we examined several control experiments. When

(4) Cinquini and co-workers[3] also report that $LiAlH_4$ was ineffective in these reductions.

(5) For example, see: White, S. S., Jr.; Kelley, H. C. *J. Am. Chem. Soc.* **1970**, *92*, 4203.

(6) Brienne, M. J.; Fouquey, C.; Jacques, J. *Bull. Soc. Chim. Fr.* **1969**, 2395. Angioloni, L.; Tramontini, M.; Fouquey, C.; Jacquet, J. *Tetrahedron* **1974**, *30*, 2801.

(7) Brown, H. C.; Zweilfel, G. *Org. React.* **1963**, *13*, 1.

Table II. Reaction of 2a and 2b with Reducing Agents

entry	C=O	reagent	2, % recov	3, % yield	3, diastereomer ratio[a]
11	2a	$LiAlH(O\text{-}t\text{-}Bu)_3$	87		
22	2a	$NaHB(O\text{-}i\text{-}Pr)_3$	100		
33	2a	K-Selectride[b]	85		
4	2b	$LiAlH_4/THF$	75	11	67:33
5	2b	$LiAlH_4/Et_2O$	63	27	70:30
6	2a	$AlCl_3/NaBH_4$[c]		71	55:45
7	2a	$BH_3\cdot N(Et)_3/BF_3\cdot Et_2O$[d]		100	50:50
8	2a	$NaBH_3CN$		100	52:48
9	2a	$(Sia)_2BH$[e]	[f]		
10	2b	$BH_3\cdot THF$ (-78 °C)	[g]	82	80:20
11	2a	$BH_3\cdot THF$ (-78 °C)		85	65:35

[a] Diastereomeric ratios estimated from ^1H NMR spectrum. [b] Brown, H. C.; Kirshnamurthy *J. Am. Chem. Soc.* **1972**, *94*, 7159. [c] Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1956**, *78*, 2585. [d] Jones, W. M. *J. Am. Chem. Soc.* **1960**, *82*, 2528. [e] Bis(1,2-dimethylpropyl)borane. [f] Only starting 2 found in undetermined amount.

Table III. β-Hydroxy Sulfoximines from the Reaction of Optically Active β-Keto Sulfoximines with Diborane

compd	R	rctn temp, °C	3, % yield[a]	approx ratio of diastereomers[b]
2a	Ph	-23		2:1
2a	Ph	-23		2:1
2a	Ph	-78	85	4:1
2a	Ph	-78	90	4:1
2c	*n*-hexyl	-23	67	3:1
2c	*n*-hexyl	-23	61	5:2
2c	*n*-hexyl	-78	75	3:1
2c	*n*-hexyl	-78	100	2:1
2d	*i*-Bu	-23		2:1
2d	*i*-Bu	-23		4:1
2d	*i*-Bu	-78	83	5:1
2d	*i*-Bu	-78		4:1
2b	*t*-Bu	-23	78	8:5
2b	*t*-Bu	-23	76	8:5
2b	*t*-Bu	-78	91	9:1
2b	*t*-Bu	-78	92	8:1

[a] Percent yield as determined by ^1H NMR analysis of product mixture. [b] Ratio of diastereomers from ^1H NMR analysis.

acetophenone in toluene at -78 °C was treated with gaseous diborane (1.5 molar equiv) for 2 h, a 20:80 mixture (96% material balance) of 1-phenylethanol and acetophenone was obtained. If, however, acetophenone is added to a toluene solution of *N,S*-dimethyl-*S*-phenylsulfoximine which has been previously treated with diborane, total reduction to 1-phenylethanol is realized. These experiments provide substance to the premise that the borane/sulfoximine complex is the actual reducing species. Concerning the possibility of intramolecular delivery of hydride in the keto sulfoximine reductions, the following experiment is noteworthy. Reaction of an equimolar mixture of (*SS*)-1-(*N*-methylphenylsulfonimidoyl)-3,3-dimethyl-2-butanone (**2b**) and racemic 2-(*N*-methylphenylsulfonimidoyl)-1-phenylethanone (**2a**) with diborane at -78 °C resulted in essentially complete conversion to the corresponding hydroxy sulfoximines. Separation of the products by silica gel chromatography led to the isolation of **3a** (68%) as a mixture of diastereomers (ratio from ^1H NMR was 87:13) and **3b** (74%), also as a mixture of diastereomers (ratio of *d,l* pairs of diastereomers by NMR was 87:13). These values correspond well with those indicated by an NMR of the initial reduction mixture and suggested that negligible diastereomeric enrichment occurred during chromatographic separation. In addition, the values were within 5% of the diastereomeric ratios generated by reduction of the individual keto sulfoximines. This fact is highly suggestive of an intramolecular reaction; but a reduction proceeding intermolecularly that is insensitive to the nature of the hydride-delivering species is also a possibility. However, after the hydroxy sulfoximines were degraded with Raney nickel, both product carbinols displayed optical activity. The optical activity of 3,3-dimethyl-2-butanol was determined to be in good agreement with that predicted from the NMR of the parent β-hydroxy sulfoximine (optical purity = 70%). This value differs by

Table IV. Optically Active Alcohols (4) from Hydrogenolysis of Optically Active β-Hydroxy Sulfoximines (3)

R	rctn temp, °C	1	% yield ROH[a]	$[\alpha]_D$ ROH[b]	% opt purity[c]	% opt purity corr[d]
Ph	-23	+168	55	-8.06	17	18
Ph	-23	+168	45	-8.84	18	20
Ph	-78	+168	75	-33.16	64	69
Ph	-78	+168	41	-30.64	63	69
n-hexyl	-23	+156	55	+1.66	17	20
n-hexyl	-23	+156	45	+2.3	23	28
n-hexyl	-78	+179	47	+4.14	42	43
n-hexyl	-78	+179	35	+2.79	29	29
i-Bu	-23	+179	42	+9.91	48	49
i-Bu	-23	+179	39	+6.66	32	33
i-Bu	-78	+174	41	+11.56	56	59
i-Bu	-78	+174	49	+13.16	64	67
t-Bu	-23	+179	36	+0.85	26	26
t-Bu	-23	+179		+0.89	27	28
t-Bu	-78	+174	41	+2.15	65	68
t-Bu	-78	+174	34	+2.09	63	66

[a] Percent yield determined by VPC analysis. [b] In solvent, see the Experimental Section. [c] Based on values listed in the Experimental Section. [d] Corrected for the optical purity of 1 in the reaction sequence.

only 3% from the average of the two values from Table IV. The optical rotation of the resulting 1-phenylethanol indicated a 3% optical yield. Although other interpretations are possible (chiral solute effect, etc.), the above results are quite consistent with an intramolecular pathway as the major process accompanied by a small intermolecular component.

The above results lead us to a study, published earlier, on the utilization of optically pure β-hydroxy sulfoximines as chiral auxillary ligands in diborane reductions of ketones.[8]

Experimental Section

General details are found in an earlier paper.[1] Raney nickel hydrogenolysis was accomplished by using the method described earlier.[1]

General Procedure for the Synthesis of β-Keto Sulfoximines (2) from the Reaction of *N,S*-Dimethyl-*S*-phenylsulfoximine (1) with Nitriles. A known quantity of *N,S*-dimethyl-*S*-phenylsulfoximine (1)[8] was added to a flame-dried flask fitted with a stirring bar, an inlet, and an outlet for nitrogen. Tetrahydrofuran (THF) was added to dissolve the sulfoximine and the solution was cooled to 0 °C. An equivalent of butyllithium was added slowly while the solution was stirred. The cooling bath was removed and the mixture allowed to stir for 15 min; a yellow suspension formed. A THF solution of the nitrile was added dropwise at room temperature. The mixture was allowed to stir under a positive nitrogen pressure overnight. In the morning a pasty solid had formed to which was added an equal volume of aqueous 6 N aqueous H_2SO_4 in order to effect dissolution. After 1 h, the layers were separated, and the THF layer was washed once with aqueous 6 N H_2SO_4. (If a third, oily layer forms, it should be combined with the aqueous layer.) The aqueous layers were combined and shaken twice with hexane; the hexane and THF layers were discarded. Aqueous 10% NaOH was added to the combined aqueous layers until a permanent turbidity was produced. The turbid solution was then extracted several times with dichloromethane. The organic extracts were washed once with saturated aqueous $NaHCO_3$, dried with $MgSO_4$, and concentrated on a rotary evaporator to yield the pure β-keto sulfoximine.

(*SS*)-2-(*N*-Methylphenylsulfonimidoyl)-1-phenylethanone (2a) was obtained (79%) from the reaction of (+)-1 with benzonitrile and displayed characteristics (mp 90–93 °C, $[\alpha]_D$ +125° (*c* 1.03, acetone)) identical with those previously reported.[9]

(*SS*)-3,3-Dimethyl-1-(*N*-methylphenylsulfonimidoyl)-2-butanone (2b) was obtained (69%) from the reaction of (+)-1 with 2,2-dimethylpropanonitrile and existed as a yellow oil: IR (neat) 1720, 1600 (br), 1260, 1160 cm^{-1} (br); ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5, Ph), 4.9–4.2 (br s, <2, SCH_2), 2.7 (br s, 3, NCH_3), 1.1 (s, 9, *t*-Bu) (^1H NMR in Me_2SO-d_6 or acetone-d_6 sharpens the resonance signal for the $SCH_2C(O)$ protons. Anal. ($C_{13}H_{19}NO_2S$) C, H.

(*SS*)-1-(*N*-Methylphenylsulfonimidoyl)-2-octanone (2c) was obtained from the reaction of (+)-1 with heptanonitrile as a yellow oil that solidified upon standing: mp 35–37 °C; IR (neat) 1720, 1610, 1260, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.0–7.3 (m, 5, Ph), 4.1 (br s, 2, SCH_2), 2.8 (br s, 5, NCH_3, $C(O)CH_2$), 2.0–0.6 (m, 11 $(CH_2)_4CH_3$). Anal. ($C_{15}H_{23}NO_2S$), C, H, N.

(*SS*)-4-Methyl-1-(*N*-methylphenylsulfonimidoyl)-2-pentanone (2d) was obtained from the condensation of (+)-1 with 3-methylbutyronitrile as a yellow oil (61%): IR (neat) 1720, 1610 (br), 1260, 1150 cm^{-1} (br); ^1H NMR ($CDCl_3$) 8.0–7.3 (m, 5, Ph), 4.1 (br s, 2, SCH_2), 2.8–2.4 (br t, 5, NCH_3, $C(O)CH_2$), 2.4–1.8 (m, 1, $CH(CH_3)_2$), 1.1–0.6 (br d, 6, $CH(CH_3)_2$). Anal. ($C_{13}H_{19}NO_2S$) C, H, N.

Decomposition of 2-(*N*-Methylphenylsulfonimidoyl)-1-phenylethanone by Diborane at Room Temperature. One gram of the keto sulfoximine **2a** was dissolved in 16 mL of dry benzene in a flask fitted with a stirring bar, an outlet for gas, and an inlet for diborane. Five equivalents of diborane, based on sulfoximine, were bubbled into the solution (see below). After 1 h, the reaction was carefully quenched with 5 mL of water. Excess 3 M aqueous NaOH (4 mL) and 30% aqueous H_2O_2 (1.5 mL) was added and the mixture was heated to reflux for 1 h. Afterward, the layers were separated, and the aqueous layer was extracted twice with small portions of ether. The organic layers were dried ($MgSO_4$) and concentrated via spinning band distillation. The residue was analyzed by VPC for 1-phenylethanol and 2-phenylethanol.

In a separate control experiment, an equimolar quantity of styrene was subjected to identical reaction and workup conditions. Analysis was also performed as described above.

Reduction of β-Keto Sulfoximines to β-Hydroxy Sulfoximines with Diborane. A. Diborane Generation. A round-bottom flask was fitted with a pressure-equalizing dropping funnel, a water-jacketed condenser, and a stirring bar. All openings were closed with septa. Nitrogen was introduced via a syringe needle through the dropping funnel and a gas outlet was provided by a syringe needle (connected to a U tube) through the septum of the condenser. After the apparatus was flame dried, the prescribed amount of $NaBH_4$ was added to the flask (see below for the calculation of the amounts of $NaBH_4$ and $BF_3{\cdot}Et_2O$), and sufficient diglyme was added to effect dissolution. An equal volume of diglyme was added to the dropping funnel followed by the prescribed amount of $BF_3{\cdot}Et_2O$.

B. Reaction Vessel. A single-necked round-bottom flask was fitted with a stirring bar and a rubber septum. A nitrogen inlet and an outlet were provided by syringe needles through the septum and the flask was charged with the β-keto sulfoximine dissolved in sufficient toluene to half-fill the flask. This flask and the diborane generator were connected with a double-tipped 18-guage transfer needle by replacing the nitrogen outlet of the generator with one end of the transfer needle and the nitrogen inlet of the reaction vessel containing the keto sulfoximine with the other end. The transfer needle was positioned so that it dipped below the surface of the toluene solution. The reaction vessel and contents were cooled to either −23 °C or −78 **C** and stirring was commenced. Addition of diborane was effected by dropwise addition of the $BF_3{\cdot}Et_2O$ solution to the stirred solution of $NaBH_4$. (A slow flow of nitrogen was required to force the diborane into the reaction vessel.) After the addition of $BF_3{\cdot}Et_2O$ was complete, the diborane generator was heated to complete the formation of diborane. The reaction vessel was then disconnected from the diborane generator and a positive nitrogen pressure maintained. After 2 h at the desired temperature, the reaction mixture was quickly poured into 5–10 mL of glacial acetic acid. After the mixture warmed to room temperature, the toluene was removed by rotary evaporation. The residue was charged with another volume of glacial acetic acid, and the mixture was stirred overnight. In the morning, the glacial acetic acid was removed on the rotary evaporator and the residue was treated with excess saturated aqueous $NaHCO_3$. The turbid aqueous layer was extracted several times with dichloromethane, and the combined extracts were dried and concentrated on the rotary evaporator to yield the β-hydroxy sulfoximine.

To these reactions, it is desired that 1.5 equiv of diborane, based on keto sulfoximine, be generated. The amounts of $NaBH_4$ and $BF_3{\cdot}Et_2O$ to be utilized were calculated according to Brown:[7] g of $NaBH_4$ = mol of sulfoximine × 1.5 × 1.8 × 38 mL $BF_3{\cdot}Et_2O$ = mol of sulfoximine × 1.5 × 2 × 142 ÷ 1.195.

(*SS*)-2-(*N*-Methylphenylsulfonimidoyl)-1-phenylethanol (3a) was obtained as a mixture of diastereomers from the reaction of (*SS*)-2 (*N*-methylphenylsulfonimidoyl)-1-phenylethanone **(2a)** with diborane at −78 **C**. The product mixture of diastereomers contained some starting material as evidenced by TLC (2:1 hexane/ethyl acetate) but was not further purified so as to avoid an alteration of the diastereomeric ratio generated (ca. 4:1 by ^1H NMR). The yield (90 ± 10%) is estimated, based upon the material balance and the ^1H NMR. TLC and spectral data compared favorably with an authentic sample prepared from the reaction of 1 with benzaldehyde.

(*SS*)-1-(*N*-Methylphenylsulfonimidoyl)-2-octanol (3c) was obtained as a mixture of diastereomers (70:30) from the reduction of (*SS*)-1-(*N*-methylphenylsulfonimidoyl)-2-octanone with diborane at −78 °C (>99%). The TLC and spectral data compared

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favorably with an authentic sample prepared from the reaction of 1 with heptanal.

(*SS*)-4-Methyl-1-(*N*-methylphenylsulfonimidoyl)-2-pentanol (3d) was obtained (ca. 83 ± 5%) as a mixture of diastereomers from the reduction of (*SS*)-4-methyl-1-(*N*-methylphenylsulfonimidoyl)-2-pentanone **(2d)** with diborane at −78 °C. TLC (2:1 hexane/ethyl acetate) indicated the presence of a small amount of starting material in the mixture, but ^{1}H NMR indicated it to be less than 5%. In order not to alter the diastereomeric ratio produced, we did not remove the contaminant but allowed it to be carried along with the hydroxy sulfoximine to the next step. TLC and spectral data compared favorably with an authentic sample prepared by the reaction of (+)-1 with 3-methylbutanal.

(*SS*)-3,3-Dimethyl-1-(*N*-methylphenylsulfonimidoyl)-2-butanol (3b) was obtained (92%) as a mixture of diastereomers (ca. 8:1) from the reduction of (*SS*)-3,3-dimethyl-1-(*N*-methylphenylsulfonimidoyl)-2-butanone **(2b)** by diborane at −78 °C. TLC (2:1 hexane/ethyl acetate) and spectral data compared favorably with an authentic sample prepared by the reaction of (+)-1 with 2,2-dimethylpropanal.

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Registry No. (+)-(*S*)-1, 33993-53-2; (*S*)-2a, 78742-26-4; (±)-2a, 80446-95-3; (*S*)-2b, 78742-25-3; (*S*)-2c, 80422-46-4; (*S*)-2d, 80422-47-5; 3a (isomer 1), 33903-51-4; 3a (isomer 2), 72174-41-5; (±)-3a (*R**,*R**), 80446-96-4; (±)-3a (*R**,*S**), 80446-97-5; 3b (isomer 1), 78742-30-0; 3b (isomer 2), 78742-34-4; 3c (isomer 1), 80422-48-6; 3c (isomer 2), 80422-49-7; 3d (isomer 1), 80422-50-0; 3d (isomer 2), 80422-51-1; (*S*)-4a, 1445-91-6; (*S*)-4b, 1517-67-5; (*S*)-4c, 6169-06-8; (*S*)-4d, 14898-80-7; benzonitrile, 100-47-0; 2,2-dimethylpropanonitrile, 630-18-2; heptanonitrile, 629-08-3; 3-methylbutyronitrile, 625-28-5; 2-phenylethanol, 60-12-8.

Reactions of 3-(Phenylthio)-3-buten-2-one with Cycloalkanones. A New Approach to Fused Phenols

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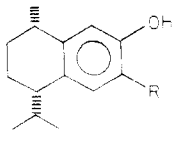
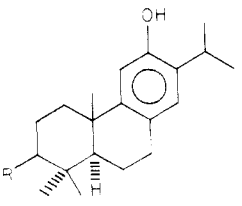
Synthesis and properties of 3-(phenylthio)-3-buten-2-one (**7**) have been described. The butenone **7** reacted with lithium cycloalkanone enolates to give ketols **14** or diketones **15** in good yields, which were easily transformed into fused phenols **17** by the treatment with *p*-toluenesulfonic acid or sodium ethoxide, respectively. Oxidative elimination of the sulfenyl group of **14a** afforded also 2-naphthol **17a**. Tetrahydronaphthalene **23**, a key intermediate of calamenene **1a** and calamenenal **1b**, was successfully synthesized by this approach by starting from *l*-carvone (**19**). Bicyclo[2.2.2]octanone **25** was obtained in the reaction of **7** with kinetic enolate of 2-cyclohexen-1-one in 84% yield.

Fused β-phenols are important structural units in natural products, for example, 7-hydroxycalamenene (**1a**), 7-hydroxycalamenenal (**1b**),[1] ferruginol (**2a**),[2] and hinokiol (**2b**).[3] Synthesis of these units has been based on the

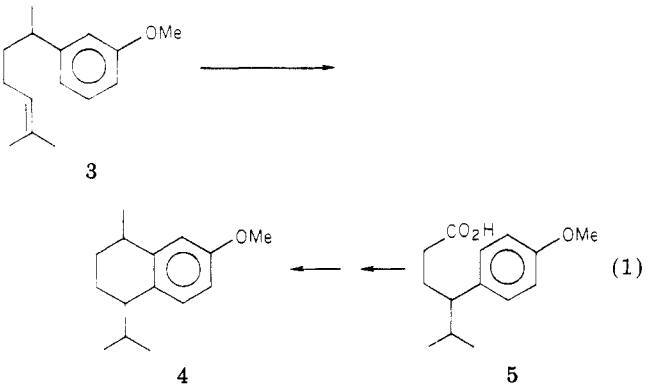


1a, R = Me
b, R = CHO



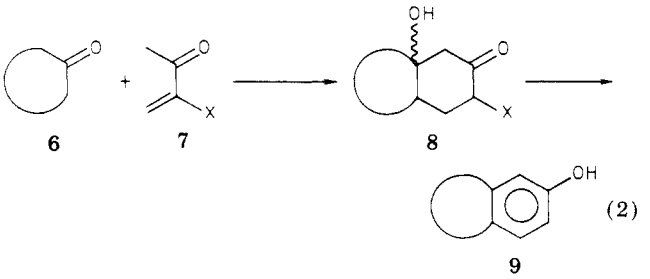
2a, R = H
b, R = OH

electrophilic substitution starting from phenol derivatives (eq 1).[4] However, this process has many limitations: (i) generation of the precursors **3** and **5** involved several nonconvergent steps; (ii) undesired products were accompanied by cationic species, and therefore yields were often low; (iii) the stereochemistry of substituents on the alicyclic



(1)

rings was not controlled. To overcome these limitations, we can envision a new strategy based on annelative method where readily available cycloalkanones **6** will react with 3-buten-2-one derivatives **7** to give ketols **8**, followed by aromatization (eq 2). This approach is closely related to



(2)

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