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Preparation of Stable, Camphor-Derived, Optically Active Allyl and Alkyl Sulfoxides and Thermal Epimerization of the Allyl Sulfoxides

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(+)-Camphor is converted by thioalkylation of the lithium enolate with allyl and alkyl *p*-toluenethiolsulfonates into *exo*-3-(allylthio)- and *exo*-3-(alkylthio)camphors, which upon reduction with diisobutylaluminum hydride give the corresponding *exo*-(allylthio)- and *exo*-(alkylthio)isoborneols. Oxidation of the sulfides with *m*-chloroperbenzoic acid gives the *exo*-(allylsulfinyl)- and *exo*-(alkylsulfinyl)isoborneols in a stereochemically pure state. The configuration at sulfur in the sulfoxides is determined by X-ray crystallography of the allyl derivative to be S_S; this configuration implies that the *exo*-hydroxyl group at C2 controls the stereochemical outcome of the oxidation. The allylic sulfoxides are stable at room temperature, but upon heating through their melting points undergo a remarkable and generally quantitative rearrangement into the R_S epimers.

Introduction

Lithiated, racemic allylic sulfoxides bearing alkyl groups at C3 or C1 undergo highly stereoselective conjugate addition to cyclopentenones to deliver vinylic sulfoxides arising from reaction through C3.[1] In seeking to extend the reaction to enantiomerically pure allylic sulfoxides, we required a number of such substrates including derivatives bearing an alkyl group at C3. A general preparation of such compounds is not available. The usual approach to optically active allylic sulfoxides is by way of the Andersen synthesis,[2] but this cannot be used to prepare 3-alkylallylic sulfoxides. One microbial oxidation of an allyl aryl sulfide to an enantiomerically pure allylic sulfoxide has been reported; it is uncertain how general this is.[3] The preparation of optically active allyl aryl sulfoxides is also complicated by their instability; the compounds racemize cleanly via a [2,3]-sigmatropic rearrangement in benzene at temperatures of 50–70 °C.[2] Preparation of alkyl allyl sulfoxides seems to be somewhat easier than that of their aryl counterparts. Oxidation of an allyl sulfide containing a steroidal group gives two epimeric sulfoxides, which are easily separated and are configurationally stable at room temperature.[4] When each sulfoxide is heated to 56 °C in benzene, epimerization at sulfur to give a 3:2 mixture of the sulfoxides takes place. (+)-(*R*)-Methyl allyl sulfoxide was prepared by Mislow[5] and it appears that this compound is stable under the conditions of its preparation. Its rate of racemization at 60.7 °C is slower than that of allyl *p*-tolyl sulfoxide by a factor of approximately 100. Certain alkyl allyl sulfoxides possess an unexpected stability in this regard. The naturally occurring alkyl allyl sulfoxide, (+)-(*S*)-allyl-*l*-cysteine, or alliin, the progenitor of the odourous principle of garlic, did not undergo epimerization at the sulfur atom during isolation and purification by crystallization from aqeuous solution.[6]

As optically active alkyl allyl sulfoxides are more stable than are aryl allyl sulfoxides, the development of a generalized approach must involve alkyl allyl sulfoxides. At the outset of this work in 1984, we considered that the alkyl group must also be *chiral*. The sulfoxide would best be prepared from a sulfide precursor and the introduction of chirality at sulfur would be carried out by *chirality-transfer* from the neighboring chiral nonallylic group during the oxidation of the sulfide. The use of a group derived from camphor, commercially available in both optically pure forms and relatively inexpensive, was therefore considered. The carbonyl group would be transformed into a hydroxyl group during preparation of the sulfide precursor. The presence of such a hydrogen-bonding donor group will control the stereochemical out-

† Department of Inorganic Chemistry.

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(6) Seebeck, E.; Stoll, A. *Helv. Chim. Acta* **1948**, *31*, 189. Block, E.; Ahmad, S.; Catalfamo, J. L.; Jain, M. K.; Apitz-Castro, R. *J. Am. Chem. Soc.* **1986**, *108*, 7045 and references therein.

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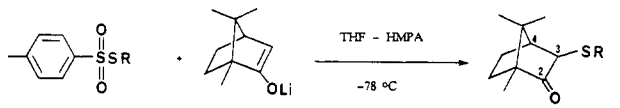
Scheme I



1 R = $-CH_2CH=CH_2$
2 R = $-CH_2CH=CHCH_3$ (*E*)
3 R = $-CH_2CH=C(CH_3)_2$
4 R = $-CH_2CH=CHC_2H_{11}$ (*E*)
5 R = $-CH_3$
6 R = $-CH_2CH_2CH_3$
7 R = $-CH_2C_6H_5$
8 R = $-CH_2CH=CH_2$
9 R = $-CH_2CH=CHCH_3$ (*E*)
10 R = $-CH_2CH=C(CH_3)_2$
11 R = $-CH_2CH=CHC_2H_{11}$ (*E*)
12 R = $-CH_3$
13 R = $-CH_2CH_2CH_3$
14 R = $-CH_2C_6H_5$

come of the oxidation of the sulfide to the sulfoxide such that one of two possible epimers is produced. Literature analogies[7,8] existing prior to the inception of the work suggested this possibility. Also, the presence of such a group adjacent to the sulfoxide may, by preferential hydrogen bonding, stabilize a single configuration at the sulfur atom in the sulfoxide over an alternative configuration which may otherwise be accessible through the [2,3]-sigmatropic rearrangement of the allylic sulfoxide.

We report here the preparation of a number of allylic sulfoxide and alkyl analogues, which effectively utilizes the foregoing concepts. Further reactions of the sulfoxides, including the conjugate addition of the derived carbanions of the allyl sulfoxides to cyclopentenone, will be reported elsewhere. Part of this work has been reported as a preliminary communication.[9]

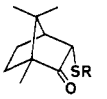
Discussion

Synthesis of 3-(Allylthio)camphor and 3-(Alkylthio)camphor Derivatives. The first step requires the stereoselective reaction of the enolate of (+)-camphor with an electrophilic reagent containing a transferable thioallyl or thioalkyl group such that the exo compound is obtained (Scheme I, below).

The enolate of (+)-camphor reacts with alkylating agents to give predominantly exo products under conditions of kinetic control and endo products under thermodynamic control.[10] However, sulfinylation of camphor enolates with alkyl arenesulfinates is reported to give predominantly *endo*-3-(arylsulfinyl)camphor derivatives.[11] The stereochemical outcome of the thioarylation of the lithium enolate of camphor with an arylsulfenyl chloride is reported to be temperature-dependent, with low temperatures favoring formation of the exo isomer.[12] With disulfide electrophiles, endo derivatives are exclusively obtained.[13,14] The lithium enolate of 4-chlorocamphor gives an endo isomer[15] upon treatment with an arenethiolsulfonate. It appears that while exo:endo ratios are sensitive to both the reaction temperature and the reactivity of the electrophile, the formation of the exo compound should be favored through use of low temperatures, short reaction times, and reactive electrophiles.

In preliminary experiments, we found that reaction of the enolate derived from (+)-camphor and lithium diisopropylamide (LDA) with diallyl disulfide gave a complex mixture of products including small amounts of the *exo*- and *endo*-(allylthio) compounds **8** and **15**. Hexamethylphosphoric triamide (HMPA) is reported to enhance the reaction of the camphor enolate with dimethyl disulfide,[14] but in the presence of the reagent both isomers were again obtained in low yield. Thus, disulfides are unsuitable as sulfenylating electrophiles. Although allylsulfenyl halides in principle would be better electrophiles, it is not possible to prepare such compounds. Accordingly, allyl and alkyl *p*-toluenethiolsulfonates were considered. The compounds **1–7** were prepared from the appropriate allyl and alkyl halide and sodium *p*-toluenethiolsulfonate.[15,16] Solutions of the lithium enolate of camphor, generated with precisely 1 equiv of LDA in THF at −78 °C, were added to the solutions of the allyl and alkyl thiotosylates **1–7** in THF containing 1 equiv of HMPA at −78 °C. After a reaction time of 1 h at −78 °C, the reaction mixtures were quenched at −78 °C. Following chromatography, the 3-(allylthio)- and 3-(alkylthio)camphor derivatives **8–14** were obtained in good yields (61–86%) (Scheme I). In most cases, exo compounds were exclusively formed; endo compounds were detected only in the crude reaction mixtures obtained from the benzyl and dimethylallyl thiotosylates.

Use of small excesses of LDA in the generation of the enolate resulted in an increase in the amount of the endo compounds. It was subsequently found that the latter could be prepared when a large excess of LDA was used. The thermodynamic *endo*-3-(allylthio)- and *endo*-3-(alkylthio)camphor derivatives **15–21** were thereby directly



15 R = $-CH_2CH=CH_2$
16 R = $-CH_2CH=CHCH_3$ (*E*)
17 R = $-CH_2CH=C(CH_3)_2$
18 R = $-CH_2CH=CHC_2H_{11}$ (*E*)
19 R = $-CH_3$
20 R = $-CH_2CH_2CH_3$
21 R = $-CH_2C_6H_5$

obtained from (+)-camphor in an essentially pure state. The exo compounds **9–14** could also be converted into mixtures rich in the corresponding endo isomers by treatment with 1.5 equiv of LDA in THF at −78 °C. An alternative attempt to prepare the endo compound **15** by the reaction of 2-propenethiolate with *exo*-bromocamphor resulted in formation of camphor and diallyl disulfide.

Assignment of stereochemistry of both exo and endo isomers was made by analysis of their 400-MHz ^1H NMR spectra. The signal for proton H3 of the *exo*-(allylthio)- and *exo*-(alkylthio)camphors **8–14** appears as a singlet at approximately δ 2.8. The lack of coupling is due to the endo orientation of H3 which has a torsion angle of approximately 90° with H4. Also the signal from H4 at approximately δ 2.1 appears as a doublet with a coupling constant between 3 and 5 Hz as it is coupled to $H5_{exo}$. The signal for H3 of the corresponding *endo*-3-(allylthio)- and *endo*-3-(alkylthio)camphors **15–21** appearing as a doublet of doublets ($J_{3,4}$ = 7–8 Hz, $J_{3,5exo}$ = 3–5 Hz) indicates that H3 is obviously exo. Fortuitously, it was found that the signals from protons H3 for the exo compounds and H4 for the endo compounds were distinct from all other pro-

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(8) Glass, R. S.; Prabhu, U. D. G.; Setzer, W. N.; Wilson, G. S. *Tetrahedron Lett.* **1982**, *23*, 2335.
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Scheme II

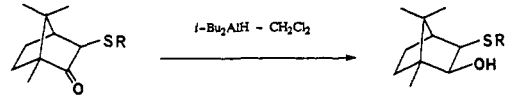


Table I. Yields and ^{1}H NMR Spectral Data of *exo*-3-(Allylthio)- and *exo*-3-(Alkylthio)isoborneols 22–28

			^{1}H NMR, δ		
compd	R	yield,[a] %	H2	H3	H4
22	allyl	76	3.55	2.93	1.83
23	(*E*)-but-2-enyl	65	3.53	2.92	1.83
24	dimethylallyl	73	3.54	2.94	1.82
25	(*E*)-oct-2-enyl	61	3.52	2.93	1.82
26	methyl	68	3.63	2.92	1.87
27	propyl	67	3.57	2.93	1.87
28	benzyl	85	3.47	2.94	1.79

[a] Diastereomer excess greater than 95% in all cases.

tons and diastereomer ratios could be determined quite simply by integration of these signals.

In summary, a route to both *exo*- and *endo*-3-(allylthio)- and *exo*- and *endo*-3-(alkylthio)camphor derivatives in high chemical yield and high diastereomeric excesses (generally >95% de) has now been developed. Providing reactive electrophiles are used, it is a relatively easy matter to produce exclusively the exo compounds under conditions of kinetic control.

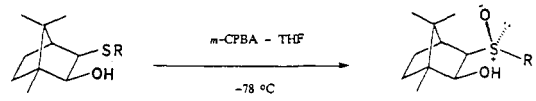
Preparation of 3-*exo*-(Allylthio)isoborneols and 3-*exo*-(Alkylthio)isoborneols. The second stage in the preparation of the sulfoxides required the stereoselective reduction of the *exo*-3-(allylthio)- and *exo*-3-(alkylthio)-camphor compounds to the diastereomerically pure *exo*-3-(allylthio)- and *exo*-3-(alkylthio)isoborneols (Scheme II, below).

Reduction of camphor with lithium aluminum hydride in ether gives a 9:1 mixture of isoborneol (*exo*-hydroxyl) and borneol (*endo*-hydroxyl).[17] Reduction of (+)-camphor-10-sulfonyl chloride gives both 10-mercaptoisoborneol and 10-mercaptoborneol in ratios ranging from 9:1 to 4:1.[18,19] Formation of the exo alcohol is favored during reduction, because underside (endo face) attack by hydride is sterically less demanding than attack on the exo face. The presence of a 3-*exo*-alkylthio group in the camphor is expected to further inhibit exo-face attack by hydride because of a larger steric constraint.

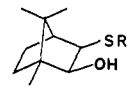
Whereas reduction of *exo*-(allylthio)camphor **8** with lithium aluminum hydride proceeded poorly, reduction with excess of sodium borohydride in methanol or ethanol gave inseparable mixtures of the *exo*-3-(allylthio)isoborneol **22** and a compound tentatively identified as the *endo*-3-(allylthio)borneol **29**, in ratios ranging from 1:1 to 3:1.[20] The related isoborneol and borneol derivatives were also formed during reduction of the thiocamphors **10** and **12**. The endo,endo compound **29**[20] obviously arises by equilibration of the starting *exo*-(allylthio)camphor **8** to the thermodynamically favored endo compound **15** brought about by methoxide or ethoxide generated in the reaction mixture, followed by reduction. To overcome the problem of the base-catalyzed epimerization attending the reduction of the exo compounds, the nonbasic diisobutylaluminum hydride in dichloromethane was used. It converted the *exo*-(allylthio)- and *exo*-(alkylthio)camphors **8–14** into the

(17) Huckel, W.; Fechtig, O. *Liebigs Ann. Chem.* **1962**, *652*, 81.
(18) Eliel, E. L.; Frazee, W. J. *J. Org. Chem.* **1979**, *44*, 3598.
(19) De Lucchi, O.; Lucchini, V.; Marchioro, C.; Valle, G.; Modena, G. *J. Org. Chem.* **1986**, *51*, 1457.
(20) Goodridge, R. J.; Haynes, R. K.; Ridley, D. D., unpublished results.

Scheme III

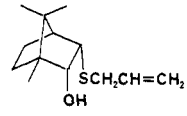


exo-(allylthio)- and *exo*-(alkylthio)isoborneols **22–28** with a high degree of stereoselectivity—no endo compounds could be detected in the crude reaction mixtures (Scheme II).



22 R = $-CH_2CH=CH_2$
23 R = $-CH_2CH=CHCH_3$ (*E*)
24 R = $-CH_2CH=C(CH_3)_2$
25 R = $-CH_2CH=CHC_5H_{11}$ (*E*)
26 R = $-CH_3$
27 R = $-CH_2CH_2CH_3$
28 R = $-CH_2C_6H_5$

The ^{1}H NMR spectra (Table I) for each of the alcohols had many similar aspects. All compounds exhibited the signal due to proton H2 as a doublet of doublets at approximately δ 3.5. Proton H2 is coupled to H3 (J = 7.5 Hz) and to OH (J = 4–5 Hz). The OH–H2 coupling is indicative of slow exchange of the hydroxyl proton due to its hindered site. The signals for H3 and H4 both appeared as doublets at approximately δ 2.9 and 1.8, respectively. When the *exo*-(allylthio)borneol **30**[20] (*endo*-hydroxyl) was



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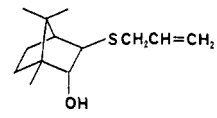

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present among the reduction products from the (allylthio)camphor **15**, this could be clearly seen from the ^{1}H NMR spectrum of the crude product mixture. The spectrum displayed a signal from proton H2 as a doublet of doublet of doublets, with couplings less than 5 Hz.

Thus far, the stereochemistry of the two reactions has been controlled. The two new chiral centers have been introduced with a degree of stereoselectivity that has enabled diastereomerically pure *exo*-3-(allylthio)- and *exo*-3-(alkylthio)isoborneols to be obtained.

Preparation of 3-*exo*-(Allylsulfinyl)- and 3-*exo*-(Alkylsulfinyl)isoborneols. Examples of asymmetric oxidation of β, γ, and δ-hydroxy sulfides have been described.[7,8,19] The stereochemical outcome of the oxidation of the diastereomeric 2-(phenylthio)-1,2-diphenyl-1-ethanols to the corresponding sulfoxides is strongly dependent upon the configuration of the carbon bearing the hydroxyl group,[7] while a δ-hydroxy sulfide is oxidized stereoselectively with either *tert*-butyl hypochlorite or with *m*-chloroperbenzoic acid.[8] During the course of the present work, it was reported that oxidation of the 10-(vinylthio)isoborneols with *m*-chloroperbenzoic acid gives the corresponding sulfoxides with diastereomeric excesses ranging from 80% to 90%.[19] On the basis of the earlier work,[7,8] we anticipated that the presence of the hydroxy group β to the sulfur in the *exo*-3-(allylthio)- and *exo*-3-(alkylthio)isoborneols **22–28** should direct the oxidation to give diastereomerically pure sulfoxides.

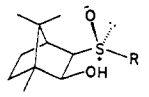
The compounds were treated with 1 equiv of *m*-chloroperbenzoic acid in THF at −78 °C. Analysis of the crude products by HPLC and/or 400-MHz ^{1}H NMR indicated that the sulfides were cleanly converted into the

Table II. Yields and ^{1}H NMR Spectral Data of (S_S)-*exo*-3-(Allylsulfinyl)- and (S_S)-*exo*-3-(Alkylsulfinyl)isoborneols 31–37

compd	R	yield,[a] %	^{1}H NMR, δ H2	H3	H4
31	allyl	60	4.09	3.06	1.70
32	(*E*)-but-2-enyl	76	4.10	3.04	1.68
33	dimethylallyl	64	4.11	3.06	1.67
34	(*E*)-oct-2-enyl	81	4.09	3.05	1.72
35	methyl	67	4.09	2.95	1.69
36	propyl	73	4.10	2.97	1.70
37	benzyl	89	4.00	2.78	1.68

[a] Diastereomer excess greater than 98% in all cases.

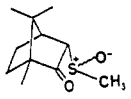
exo-3-(allylsulfinyl)- and *exo*-3-(alkylsulfinyl)isoborneol derivatives **31–37** in good yields (Scheme III and Table II).



31 R = $-CH_2CH=CH_2$
32 R = $-CH_2CH=CHCH_3$ (*E*)
33 R = $-CH_2CH=C(CH_3)_2$
34 R = $-CH_2CH=CHC_5H_{11}$ (*E*)
35 R = $-CH_3$
36 R = $-CH_2CH_2CH_3$
37 R = $-CH_2C_6H_5$

These were easily purified by recrystallization; in the cases of the allylic sulfoxides **31–34** which were less stable (see below), this was carried out at room temperature.

The S_S configuration at sulfur was confirmed by an X-ray crystallographic study on the allylic sulfoxide **31**, the ORTEP plot from which is presented in Figure 1.[21] The configuration at sulfur indicates that the hydroxyl group directs the *m*-chloroperbenzoic acid to attack the *pro-S* lone pair on the sulfur atom. Results of the oxidation of other sulfides also tend to support this. Thus, whereas oxidation of *endo*-3-(methylthio)camphor (**19**) with sodium metaperiodate in aqueous methanol gave a 78:22 mixture of epimers of the unstable sulfoxides **38**, with *m*-chloro-



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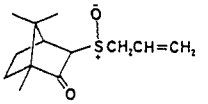

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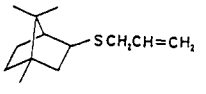

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perbenzoic acid in dichloromethane the ratio was 59:41.[22] Oxidation of the *exo*-(allylthio)camphor **8** with *m*-chloroperbenzoic acid in dichloromethane at −78 °C afforded the epimeric sulfoxides **39** in a ratio of 4:1. In THF, the ratio became 99:1, which represents a surprisingly high diastereoselection. However, we have prepared the deshydroxy sulfide **40** and have shown that its oxidation under the foregoing conditions delivers a mixture of (S_S)- and (R_S)-sulfoxides in a ratio of 59:41.[23]

Epimerization of the 3-*exo*-(Allylsulfinyl)isoborneols. The allylic sulfoxides **31–34** are easily manip-

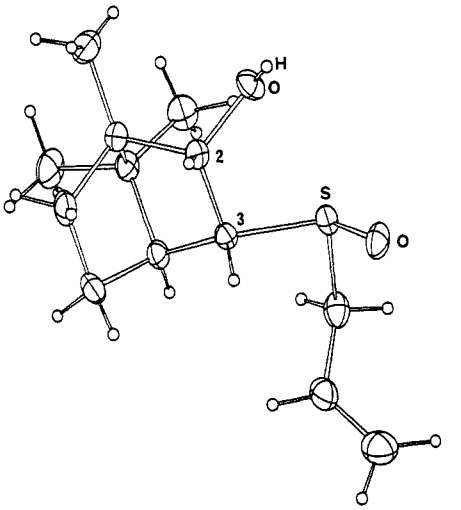
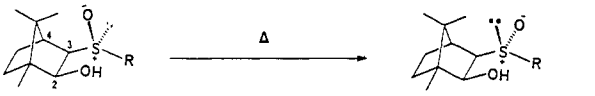


Figure 1. ORTEP plot of (1*R*,2*S*,S_S)-*exo*-3-(prop-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**31**).

Scheme IV



31 R = $-CH_2CH=CH_2$
32 R = $-CH_2CH=CHCH_3$ (*E*)
33 R = $-CH_2CH=C(CH_3)_2$
34 R = $-CH_2CH=CHC_5H_{11}$ (*E*)

41 R = $-CH_2CH=CH_2$
42 R = $-CH_2CH=CHCH_3$ (*E*)
43 R = $-CH_2CH=C(CH_3)_2$
44 R = $-CH_2CH=CHC_5H_{11}$ (*E*)

ulated without apparent epimerization at room temperature. The most stable of these sulfoxides, compound **31**, is unaffected on storage at room temperature for several weeks. However, upon heating the compound as a solution in dideuteriotetrachloroethane at 110 °C for 3 h, an equilibrium mixture consisting of **31** and its epimer **41** in the ratio of 65:35 (as assessed by ^{1}H NMR spectroscopy) was obtained. There was no detectable epimerization of **31** below 100 °C.

However, it was found that the pure epimer **41** could be obtained from **31** in a remarkably simple manner (Scheme IV). When compound **31** was heated through its melting point, 134–135 °C, to 145 °C, the melt slowly solidified to produce *quantitatively* the epimer **41**, mp 171–174 °C; no detectable amount of the original sulfoxide remained at the end of the process. It seems that as compound **31** melts, equilibration with **41** occurs in the melt. As the latter compound has a higher melting point, it precipitates as a solid from the melt, and so the equilibrium is drawn toward compound **41**. The allylic sulfoxides **32** and **33** could also be rearranged in a similar fashion, although in these cases epimerization took place at lower temperatures. When sulfoxide **32** (mp 91–93 °C) was heated through its melting point to 110 °C for 20 min, solidification was associated with formation of the higher melting epimer **42** (mp 175–177 °C). This was also the case with sulfoxide **33** (mp 84–86 °C); this when heated at 90 °C until complete crystallization had taken place was converted entirely into its higher melting epimer **43** (mp 199–200 °C). The sulfoxides **41–43** could be handled without special precautions at room temperature, although these did appear to be less stable than the allylic sulfoxide **31** with respect to protracted storage at room temperature.

The sulfoxides **31**, **32**, and **34** could be recrystallized without change, but when attempts were made to recrystallize the dimethylallyl sulfoxide **33** from boiling light petroleum ether (bp 60–70 °C), stereomutation occurred in a spectacular way. Immediately upon dissolution of the

(21) Crystal data for **31** are given in the supplementary material.
(22) These keto sulfoxides were unstable and after a matter of days had decomposed completely to camphorquinone.
(23) The preparation of **40** and its oxidation will be described in detail elsewhere.

Table III. Yields and ^{1}H NMR Spectral Data of (R_S)-*exo*-3-(Allylsulfinyl)isoborneols 41–44

compd	R	yield, %	% de	^{1}H NMR, δ H2	H3	H4
41	allyl	>95	>98	3.84	3.02	2.38
42	(*E*)-but-2-enyl	>95	>98	3.83	2.98	2.36
43	dimethylallyl	>95	>98	3.86	3.01	2.32
44	(*E*)-oct-2-enyl	>95	80	3.82	3.02	2.39

sulfoxide in the hot solvent, precipitation occurred; the precipitate, formed in quantitative yield, was found to consist of a mixture of the epimer **43** (96%) and the starting sulfoxide **33** (4%). Clearly, the epimer formed upon rearrangement is less soluble than the starting sulfoxide in light petroleum ether, and thus the ensuing precipitation of the epimer draws the equilibrium toward formation of this compound.

Finally, when the (*E*)-octenyl sulfoxide **34** (mp 82–84 °C) was heated above its melting point for several hours, no crystallization took place. Analysis of the melt showed it to be a 90:10 mixture of the (*E*)-octenyl sulfoxides **44** and **34**, as established by ^{1}H NMR spectroscopy and by HPLC. The result indicates that in order for the epimerization to proceed to completion, the epimer must have a higher melting point than the original compound, so that the equilibrium is drawn toward formation of the epimer by the deposition of this higher melting, solid epimer from the melt of the original sulfoxide. It seems that in solution or in a melt where precipitation does not take place, the actual position of the equilibrium between the two epimers does not exclusively favor one of these. The efficiency of these epimerization processes is quite remarkable and they do not have any parallel in the literature. It is also appropriate to note that we have also prepared a related series of allylic sulfoxides by oxidation of allyl sulfides derived from 10-mercaptoisoborneol;[24] these sulfoxides cannot be converted into their epimers in the manner described for the sulfoxides **31–34**.

An examination of the ^{1}H NMR spectra of the S_S sulfoxides **31–37** and the R_S sulfoxides **41–44** (Tables II and III) allows a number of points to be made. The spectra of sulfoxides **31–37** all have similar aspects. Chemical shifts of the signals for the protons H2, H3, and H4 occur at approximately δ 4.1, 3.1, and 1.7, respectively, and the shifts are consistent for each compound in this series. The signal from proton H2 appears as a doublet of doublets with $J_{2,3}$ = 7–7.5 Hz and $J_{2,OH}$ = 3–5 Hz. The couplings between H2 and H3 are consistent with a cis orientation of these protons. The resonance from H4 is also a doublet with $J_{4,5exo}$ = 4–5 Hz; as H4 is not coupled to H3, this demonstrates that H3 is endo.

The R_S sulfoxides **41–44**, like their S_S counterparts **31–34**, have similar shifts which are consistent for each in the series. The signals from protons H2, H3, and H4 have chemical shifts of approximately δ 3.8, 3.0, and 2.3, respectively. The proposals made for the S_S sulfoxides also apply to the R_S sulfoxides in regard to coupling constants and proof of structure. Of particular note in the determination of configuration at sulfur is the chemical shifts exhibited by H4 in both the S_S and R_S sulfoxides. For the S_S sulfoxides **31–34**, H4 appears at approximately δ 1.7 and for the R_S isomers **41–44**, H4 is at about δ 2.3. The chemical shift difference implies that the oxygen of the R_S sulfoxides lies next to proton H4 in space as this would account for the downfield shift of its signal in the ^{1}H NMR spectrum. The signal from proton H4 in the S_S sulfoxides is upfield to that in the spectrum of the R_S isomers, and hence the oxygen lies away from this proton in the S_S sulfoxides. This phenomenon allows the determination of the diastereomeric purity of the compounds to be carried out by simple integration of the relevant proton signals in the ^{1}H NMR spectrum and also gives information about the stereochemistry of the sulfoxide group in compounds of this type.

(24) Haynes, R. K.; Kniha, J. K.; Ridley, D. D., unpublished work. The allylic sulfoxide in this series has been independently prepared.[25]

Conclusion

We have described herein a method for the preparation of optically active sulfoxides that commences with (+)-camphor and that relies in the final step upon the efficient transfer of chirality from the neighboring chiral and optically active bornyl group during oxidation of the sulfide precursors. As the sulfoxides are obtained in an optically pure state, the method is clearly a useful one. Use of (−)-camphor in the sequence will enable the enantiomers of the sulfoxides described herein to be prepared. The extraordinary thermal epimerization of the allylic sulfoxides, however, does enable the preparation of optically pure and relatively stable allylic sulfoxides possessing opposite configurations at the sulfur atom to be easily carried out without recourse to the use of (−)-camphor. Because of the untoward thermal properties displayed by the allylic sulfoxides **31–34**, we have examined the kinetics of the rearrangement reaction in some detail. This work, and the results of an examination of the conjugate addition reactions of the derived dianions with cyclopentenones,[9] will be described separately.

Experimental Section

General Aspects. Melting points were recorded on a Reichert melting point hot stage and are uncorrected. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter using a 1.00-dm cell at 25 °C. ^{1}H NMR spectra were recorded on a Bruker WM 400 spectrometer with chemical shifts (δ) given in ppm from internal TMS. High resolution mass spectra were recorded at 70 eV on an AEI MS9 spectrometer connected to a DS 390 data handling system. Microanalyses were performed by the Australian Mineral Development Laboratories, Melbourne. Merck silica gel 60 (230–400-mesh ASTM) was used for flash chromatography. Analytical HPLC was carried out with a Waters Model 6000A pump with U6K injector, R-401 refractive index detector, and Model 450 variable wavelength UV detector. Analytical reverse-phase HPLC was performed with a Du Pont Zorbax ODS 4.6 mm × 25 cm column. Butyllithium was standardized by titration,[26] and THF and other solvents and reagents were purified as described elsewhere.[27]

Preparation of Allyl and Alkyl *p*-Toluenethiolsulfonates 1–7. The following were prepared according to a general method:[16] prop-2-enyl **1** [pale yellow oil, bp 140–145 °C (0.01 mm) (Kugelrohr) [lit.[16,30] bp 126–129 °C (0.03 mm)]], methyl **5** [colorless crystals, mp 56–58 °C (lit.[28] mp 58 °C) from ethanol], propyl **6** [colorless oil, bp 150–155 °C (0.7 mm) (Kugelrohr) [lit.[16] bp 145 °C (0.1 mm)]], and benzyl **7** [needles, mp 57–59 °C (lit.[29] mp 60 °C) from ethanol]. Also prepared by this method were (*E*)-but-2-enyl **2** [colorless oil; ^{1}H NMR δ 7.80 (2 H, dm, *J* = 8.4 Hz), 7.34 (2 H, dm, *J* = 8.4 Hz), 5.63 (1 H, m H2), 5.32 (1 H, m, H3), 3.63 (2 H, dm, *J* = 7.3 Hz, H1), 2.45 (3 H, s, CH_3), 1.59 (3 H, dm, *J* = 6.4 Hz, H4); HRMS calcd for $C_{11}H_{14}O_2S_2$ 242.0435, found 242.0427], 3-methylbut-2-enyl **3** [colorless oil; ^{1}H NMR δ 7.73 (2 H, d, *J* = 9.5 Hz), 7.26 (2 H, d, *J* = 9.5 Hz), 5.08 (1 H, ddq, *J* = 8.0, 8.0, 1.5 Hz, H2), 3.65 (2 H, d, *J* = 8.0 Hz, H1), 2.45 (3 H, s,

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CH_3), 1.64 (3 H, s, CH_3), 1.60 (3 H, s, CH_3); HRMS calcd for $C_{12}H_{16}O_2S_2$ 256.0592, found 256.0586], and (*E*)-oct-2-enyl **4** [colorless oil, bp 150–155 °C (0.5 mm) (Kugelrohr); ^1H NMR δ 7.82 (2 H, d, J = 8.0 Hz), 7.35 (2 H, d, J = 8.0 Hz), 5.64 (1 H, m, H2), 5.33 (1 H, m, H3), 3.65 (2 H, dm, J = 6.5 Hz, H1), 2.44 (3 H, s, CH_3), 2.2–1.7 (2 H, m, H4), 1.5–1.0 (6 H, m, H5, H6, H7), 0.85 (3 H, t, J = 7.2 Hz, H8). Anal. Calcd for $C_{15}H_{22}O_2S_2$: C, 60.3; H, 7.4; S, 21.5. Found: C, 59.9; H, 7.5; S, 21.1].

Preparation of 3-(Allylthio)camphor and 3-(Alkylthio)-camphor Derivatives 8–21. (1*R*)-*exo*-3-(2′-Propenylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (8). To a solution of lithium diisopropylamine (LDA), prepared from butyllithium (1.3 mL, 2.5M in hexane) and diisopropylamine (0.46 mL) in THF (20 mL) at −78 °C under nitrogen was added (+)-camphor (0.5 g, 3.3 mmol) in THF (5 mL). The solution was stirred for 1.5 h and added via a cannula to a solution of the allyl thiotosylate 1 (0.9 g, 4.0 mmol) and HMPA (1.8 g, 10.0 mmol) in THF (10 mL) at −78 °C under nitrogen. The resulting mixture was stirred at this temperature for 2 h. It was quenched at −78 °C with saturated aqueous sodium hydrogen sulfate (30 mL) and extracted with ether (3 × 30 mL). The combined ether extracts were washed with hydrochloric acid (3 M, 3 × 50 mL) and saturated aqueous sodium hydrogen carbonate (3 × 50 mL) and dried ($MgSO_4$) and the solvent was removed to leave an oil. The crude product was purified by chromatography with 3:97 ether:light petroleum ether to give the product **8** (575 mg, 78%) as a yellow oil, bp 105–107 °C (0.3 mm) (Kugelrohr), $[\alpha]_D$ +75° (*c* 2.0, acetone): ^1H NMR δ 5.82 (1 H, m, H2′), 5.11 (1 H, m, H3′), 3.45 (1 H, ddm, J = 13.5, 7.8 Hz, H1′), 3.26 (1 H, ddm, J = 13.5, 6.5 Hz, H1′), 2.82 (1 H, s, H3), 2.07 (1 H, d, $J_{4,5exo}$ = 4.0 Hz, H4), 2.03, 1.64 and 1.43 (4 H, m, H5, H6), 0.98 (3 H, s, CH_3), 0.92 (6 H, s, 2 × CH_3); HRMS calcd for $C_{13}H_{20}OS$ 224.1235, found 224.1239.

(1*R*,2′*E*)-*exo*-3-(But-2′-enylthio)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (9). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the (*E*)-but-2-enyl thiotosylate **2** (0.97 g, 4.0 mmol) was purified by chromatography with 3.5:96.5 ether:light petroleum ether to give the product **9** (640 mg, 81%) as a colorless oil, bp 120–125 °C (0.4 mm) (Kugelrohr), $[\alpha]_D$ +90.6° (*c* 2.0, acetone): ^1H NMR δ 5.57 (1 H, m, H2′), 5.48 (1 H, m, H3′), 3.37 (1 H, ddm, J = 13.5, J = 7.8 Hz, H1′), 3.24 (1 H, ddm, J = 13.5, J = 6.6 Hz, H1′), 2.82 (1 H, s, H3), 2.07 (1 H, m, H4), 2.03, 1.65, 1.49, 1.40 (4 H, m, H5, H6), 1.71 (3 H, dm, J = 6.0 Hz, H4′), 0.97 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.92 (3 H, s, CH_3). Anal. Calcd for $C_{14}H_{22}OS$: C, 70.6; H, 9.3. Found: C, 70.4; H, 9.5.

(1*R*)-*exo*-3-[(3′-Methylbut-2′-enyl)thio]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (10). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the dimethylallyl thiotosylate **3** (1.0 g, 4.0 mmol) was purified by chromatography with 4:96 ether:light petroleum ether to give the product **10** (720 mg, 86%) as a colorless oil, bp 180–190 °C (0.7 mm) (Kugelrohr), $[\alpha]_D$ +65.8° (*c* 2.0, acetone): ^1H NMR δ 5.25 (1 H, ddm, J = 8.4, J = 7.6 Hz, H2′), 3.47 (1 H, ddm, J = 13.2, J = 8.4 Hz, H1′), 3.31 (1 H, ddm, J = 13.2, J = 7.6 Hz, H1′), 2.81 (1 H, s, H3), 2.09 (1 H, d, $J_{4,5exo}$ = 4.2 Hz, H4), 1.75 (3 H, s, CH_3), 1.67 (3 H, s, CH_3), 2.03, 1.59, 1.46, 1.36 (4 H, m, H5, H6), 0.98 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.92 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{24}OS$: C, 71.4; H, 9.6. Found: C, 71.2; H, 9.5.

(1*R*,2′*E*)-*exo*-3-(Oct-2′-enylthio)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (11). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the (*E*)-octenyl thiotosylate **4** (1.2 g, 4.0 mmol) was purified by chromatography with 5:95 ether:light petroleum ether to give the product **11** (710 mg, 72%) as a colorless oil, bp 160–165 °C (0.5 mm), $[\alpha]_D$ + 65.8° (*c* 1.0, acetone): ^1H NMR δ 5.55 (1 H, m, H1′), 5.44 (1 H, m, H2′), 3.39 (1 H, ddm, J = 13.5, J = 7.8 Hz, H1′), 3.23 (1 H, ddm, J = 13.5, J = 6.5 Hz, H1′), 2.84 (1 H, s, H3), 2.04, 1.64, 1.50–1.25 (13 H, m, H4, H5, H6, H4′, H5′, H6′, H7′), 0.97 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.88 (3 H, t, J = 7.0 Hz, H8′); HRMS calcd for $C_{18}H_{30}OS$ 294.2017, found 294.2017. Anal. Calcd for $C_{18}H_{30}OS$: C, 73.4; H, 10.3. Found: C, 73.1; H, 10.0.

(1*R*)-*exo*-3-(Methylthio)-1,7,7-trimethylbicyclo[2.2.1]-heptan-2-one (12). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the methyl thiotosylate **5** (0.8 g, 4.0 mmol) was purified by chromatography with 3:97 ether:light petroleum ether to give the product **12** (490 mg, 74%) as a colorless oil, bp 135–140 °C (0.5 mm) (Kugelrohr), $[\alpha]_D$ +93.3° (*c* 2.0, acetone): ^1H NMR δ 2.80 (1 H, s, H3), 2.36 (3 H, s, SCH_3), 2.13 (1 H, d, $J_{4,5exo}$ = 4.1 Hz, H4), 2.06, 1.66, and 1.46 (4 H, m, H5, H6), 1.00 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.93 (3 H, s, CH_3). Anal. Calcd for $C_{11}H_{18}OS$: C, 66.6; H, 9.1. Found: C, 66.8; H, 8.8.

(1*R*)-*exo*-3-(Propylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (13). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the propyl thiotosylate **6** (0.92 g, 4.0 mmol) was purified by chromatography with 2:98 ether:light petroleum ether to give the product **13** (460 mg, 61%) as a colorless oil, bp 190–195 °C (1 mm) (Kugelrohr), $[\alpha]_D$ +83.9° (*c* 2.0, acetone): ^1H NMR δ 2.81 (1 H, s, H3), 2.73 (2 H, t, J = 7.4 Hz, H1′), 2.13 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 2.06, 1.64, and 1.48 (each 2 H, m, H5, H6, H2′), 1.00 (3 H, t, J = 7.4 Hz, H3″), 0.97 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.92 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}OS$: C, 69.0; H, 9.8. Found: C, 69.0; H, 9.5.

(1*R*)-*exo*-3-(Benzylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (14). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the benzyl thiotosylate **7** (1.1 g, 4.0 mmol) was purified by chromatography with 2:98 ether:light petroleum ether to give the product **14** (730 mg, 80%) as prisms, mp 73–75 °C, from ethyl acetate/light petroleum ether, $[\alpha]_D$ +126.6° (*c* 3.0, acetone): ^1H NMR δ 7.37–7.22 (5 H, m, C_6H_5), 4.01 (1 H, d, J = 13.0 Hz, H1′), 3.93 (1 H, d, J = 13.0 Hz, H1′), 2.74 (1 H, s, H3), 1.93, 1.60, 1.41, 1.23 (5 H, m, H4, H5, H6), 0.98 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.89 (3 H, s, CH_3). Anal. Calcd for $C_{17}H_{22}OS$: C, 74.4; H, 8.1. Found: C, 74.4; H, 7.9.

(1*R*)-*endo*-3-(Prop-2′-enylthio)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (15). (+)-Camphor (0.5 g, 3.3 mmol) in THF (5 mL) was added to a solution of LDA, prepared from butyllithium (2.9 mL, 2.5M in hexane) and diisopropylamine (0.97 mL) in THF (20 mL) at −78 °C under nitrogen. The solution was stirred for 1.5 h and passed via a cannula into a solution of the allyl thiotosylate 1 (0.91 g, 4.0 mmol) and HMPA (1.8 g, 10.0 mmol) in THF (10 mL). The resulting solution was stirred at −78 °C for 1 h and then for 3 h at room temperature. It was poured into water (30 mL) and extracted with ether (3 × 30 mL). The combined ether extracts were washed with hydrochloric acid (3 M, 3 × 30 mL) and saturated aqueous sodium hydrogen carbonate (3 × 30 mL), then dried ($MgSO_4$), and evaporated under reduced pressure. The product was purified by chromatography with 3:97 ether:light petroleum ether to yield the product **15** (588 mg, 80%) as a pale yellow oil, bp 80 °C (0.1 mm) (Kugelrohr), $[\alpha]_D$ +21.9° (*c* 4.0, acetone): ^1H NMR δ 5.82 (1 H, m, H2′), 5.15 (2 H, m, H3′), 3.46 (1 H, ddm, J = 13.5, J = 7.5 Hz, H1′), 3.24 (1 H, ddm, J = 13.5, J = 6.8 Hz, H1′), 3.43 (1 H, dd, $J_{3,4}$ = 4.5, $J_{3,5exo}$ = 2.0 Hz, H3), 2.15 (1 H, dd, $J_{4,3}$ = 4.5, $J_{4,5exo}$ = 4.5 Hz, H4), 1.94–1.39 (4 H, m, H5, H6), 1.01 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.90 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{20}OS$: C, 69.6; H, 8.9; S, 14.3. Found: C, 69.4; H, 9.0; S, 14.6.

(1*R*,2′*E*)-*endo*-3-(But-2′-enylthio)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (16). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the (*E*)-but-2-enyl thiotosylate **2** (0.97 g, 4.0 mmol) was purified by chromatography with 3:97 ether:light petroleum ether to give the product **16** (610 mg, 77%) as a colorless oil, bp 130–135 °C (0.5 mm) (Kugelrohr), $[\alpha]_D$ +0.6° (*c* 4.0, acetone): ^1H NMR δ 5.58 (1 H, m, H2′), 5.47 (1 H, m, H3′), 3.44 (1 H, dd, $J_{3,4}$ = 4.5, $J_{3,5exo}$ = 2.0, J = 0.8 Hz, H3), 3.39 (1 H, ddm, J = 13.3, J = 7.8 Hz, H1′), 3.20 (1 H, ddm, J = 13.3, J = 6.5 Hz, H1′), 2.12 (1 H, dd, $J_{4,3}$ = 4.5, $J_{4,5exo}$ = 4.5 Hz, H4), 1.89, 1.78, 1.44 (4 H, m, H5, H6), 1.70 (3 H, dm, J = 6.3 Hz, H4′), 1.01 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.89 (3 H, s, CH_3). Anal. Calcd for $C_{14}H_{22}OS$: C, 70.6; H, 9.3. Found: C, 70.9; H, 9.5.

(1*R*)-*endo*-3-[(3′-Methylbut-2′-enyl)thio]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (17). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the dimethylallyl thiotosylate **3** (1.0 g, 4.0 mmol) was purified by chromatography with 5:95 ether:light petroleum ether to give the product **17** (620 mg, 75%) as a colorless oil, bp 220–225 °C (0.7 mm) (Kugelrohr), $[\alpha]_D$ +11.9° (*c*, 1.0, acetone): ^1H NMR δ 5.25 (1 H, ddm, J = 8.5, J = 7.3 Hz, H2′), 3.50 (1 H, dd, J = 13.0, J = 8.5 Hz, H1′), 3.25 (1 H, dd, J = 13.0, J = 7.3 Hz, H1′), 3.38 (1 H, ddd, $J_{3,4}$ = 4.5, $J_{3,5exo}$ = 1.8, J = 0.5 Hz, H3), 2.14 (1 H, dd, $J_{4,3}$ = 4.5, $J_{4,5exo}$ = 4.0 Hz, H4), 1.88, 1.79, 1.65, 1.44 (4 H, m, H5, H6), 1.75 (3 H, s, CH_3), 1.65, (s, CH_3), 1.01 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{24}OS$: C, 71.4; H, 9.6. Found: C, 71.1; H, 9.7.

(1*R*,2′*E*)-*endo*-3-(Oct-2′-enylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (18). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the (*E*)-octenyl thiotosylate **4** (1.2 g, 4.0 mmol) was purified by chromatography with 2:98 ether:light petroleum ether to give the product **18** (760 mg, 78%) as a colorless oil, bp 240–250 °C (1.2 mm) (Kugelrohr), $[\alpha]_D$ −0.9° (*c* 1.0, acetone): ^{1}H NMR δ 5.57 (1 H, m, H2′), 5.42 (1 H, m, H3′), 3.45 (1 H, ddd, $J_{3,4}$ = 4.7, $J_{3,5exo}$ = 2.0, *J* = 0.8 Hz, H3), 3.40 (1 H, ddm, *J* = 13.5, *J* = 7.6 Hz, H1′), 3.18 (1 H, ddm, *J* = 13.5, *J* = 6.8 Hz, H1′), 2.11 (1 H, dd, $J_{4,3}$ = 4.7, $J_{4,5exo}$ = 4.0 Hz, H4), 2.03 (2 H, m, H4′), 1.89, 1.78, 1.69, 1.44, 1.39–1.23 (10 H, m, H5, H6, H5′, H6′, H7′), 1.01 (3 H, s, CH_3), 0.92 (3 H, s, CH_3), 0.88 (3 H, s, CH_3), 0.88 (3 H, t, *J* = 7.0 Hz, H8′). Anal. Calcd for $C_{18}H_{30}OS$: C, 73.4; H, 10.3. Found: C, 73.1; H, 10.2.

(1*R*)-*endo*-3-(Methylthio)-1,7,7-bicyclo[2.2.1]heptan-2-one (19). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the methyl thiotosylate **5** (0.8 g, 4.0 mmol) according to the foregoing method was purified by chromatography with 5:95 ether:light petroleum ether to give the product as a colorless oil (580 mg, 89%), bp 70–72 °C (0.5 mm) (Kugelrohr) [lit.[13,31] bp 83–84 °C (1 mm)]: ^{1}H NMR (90 MHz) δ 3.15 (1 H, d, $J_{3,4}$ = 4.9 Hz, H3), 2.25 (3 H, s, CH_3), 2.2–1.2 (5 H, m, H4, H5, H6), 1.00 (3 H, s, CH_3), 0.88 (3 H, s, CH_3), 0.85 (3 H, s, CH_3).

(1*R*)-*endo*-3-(Propylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (20). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the propyl thiotosylate **6** (0.92 g, 4.0 mmol) was purified by chromatography with 5:95 ether:light petroleum ether to give the product **20** (560 mg, 75%) as a colorless oil, bp 145–150 °C (0.5 mm) (Kugelrohr), $[\alpha]_D$ +33.6° (*c* 1.0, acetone): ^{1}H NMR δ 3.41 (1 H, ddd, $J_{3,4}$ = 4.5, $J_{3,5exo}$ = 2.0, *J* = 0.5 Hz, H3), 2.69 (2 H, t, *J* = 7.4 Hz, H1′), 2.17 (1 H, dd, $J_{4,3}$ = 4.5, $J_{4,5exo}$ = 4.0 Hz, H4), 1.91, 1.76, 1.64, 1.42 (6 H, m, H5, H6, H2′), 1.00 (3 H, t, *J* = 7.4 Hz, H3′), 1.01 (3 H, s, CH_3), 0.91 (3 H, s, CH_3), 0.90 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}OS$: C, 69.0; H, 9.8. Found: C, 69.1; H, 9.9.

(1*R*)-*endo*-3-(Benzylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (21). The crude product obtained from (+)-camphor (0.5 g, 3.3 mmol) and the benzyl thiotosylate **7** (1.1 g, 4.0 mmol) was purified by chromatography with 5:95 ether:light petroleum ether to give the product **21** (660 mg, 73%) as a colorless oil, bp 250 °C (1 mm) (Kugelrohr), $[\alpha]_D$ −64.0° (*c* 0.5, acetone): ^{1}H NMR δ 7.39–7.23 (5 H, m, C_6H_5), 4.03 (1 H, d, *J* = 12.9 Hz, H1′), 3.87 (1 H, d, *J* = 12.9 Hz, H1′), 3.30 (1 H, ddd, $J_{3,4}$ = 4.6, $J_{3,5exo}$ = 1.9, *J* = 0.8 Hz, H3), 2.01 (1 H, dd, $J_{4,3}$ = 4.6, $J_{4,5exo}$ = 3.8 Hz, H4), 1.86, 1.75, 1.68, 1.46 (4 H, m, H5, H6), 0.98 (3 H, s, CH_3), 0.91 (3 H, s, CH_3), 0.79, (s, CH_3). Anal. Calcd for $C_{17}H_{22}OS$: C, 74.4; H, 8.1. Found: C, 74.3; H, 7.7.

Preparation of 3-*exo*-(Allylthio)isoborneols and 3-*exo*-(Alkylthio)isoborneols 22–28. (1*R*,2*S*)-*exo*-3-(Prop-2′-enylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (22). Diisobutylaluminum hydride (25% in toluene, 2.0 mL, 3.5 mmol) was added dropwise at room temperature to a solution of *exo*-3-(allylthio)camphor **8** (500 mg, 2.2 mmol) in dichloromethane (10 mL), and the mixture was stirred for 30 min. The reaction mixture was then poured into a saturated ammonium chloride solution (30 mL) and extracted into light petroleum ether (3 × 40 mL). The combined extracts were washed with hydrochloric acid (3 M, 2 × 30 mL) and saturated sodium hydrogen carbonate solution (3 × 30 mL) and dried ($MgSO_4$), and the solvent was removed. The crude product was purified by chromatography with 3:97 ether:light petroleum ether and distilled to give the product **22** as a colorless oil (430 mg, 86%), bp 100 °C (0.04 mm), $[\alpha]_D$ +10.6° (*c* 2.0, acetone): ^{1}H NMR δ 5.81 (1 H, m, H2′), 5.10 (2 H, m, H3′), 3.55 (1 H, d, $J_{2,3}$ = 7.1 Hz, H2), 3.10 (2 H, dm, *J* = 7.2 Hz, H1′), 2.93 (1 H, d, $J_{3,2}$ = 7.1 Hz, H3), 2.81 (1 H, br s, OH), 1.83 (1 H, d, $J_{4,5exo}$ = 4.0 Hz, H4), 1.77 (1 H, dddd, $J_{5exo,5endo}$ = 11.0, $J_{5exo,6exo}$ = 11.0, $J_{5exo,4}$ = 4.0, $J_{5exo,6endo}$ = 4.0 Hz, H5exo), 1.48 (1 H, m, H6exo), 1.10 (1 H, m, H5endo, H6endo), 1.00 (1 H, s, CH_3), 0.96 (3 H, S, CH_3), 0.78 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}OS$: C, 69.0; H, 9.8; S, 14.2. Found: C, 68.7; H, 9.5; S, 13.8.

(1*R*,2*S*,2′*E*)-*exo*-3-(But-2′-enylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (23). The crude product obtained from the *exo*-3-(but-2′-enylthio)camphor **9** (500 mg, 2.1 mmol) and diisobutylaluminum hydride (3.0 mmol) was submitted to chromatography with 2.5:97.5 ether:light petroleum ether and distilled to give the product **23** as a colorless oil (330 mg, 65%), bp 210 °C (0.8 mm), $[\alpha]_D$ +3.0° (*c* 2.0, acetone): ^{1}H NMR 5.55 (1 H, m, H2′), 5.44 (1 H, m, H3′), 3.53 (1 H, dd, $J_{2,3}$ = 7.5, $J_{2,OH}$ = 4.3 Hz, H2), 3.06 (2 H, dm, *J* = 7.1 Hz, H1′), 2.92 (1 H, d, $J_{3,2}$ = 7.5 Hz, H3), 2.90 (1 H, d, $J_{OH,2}$ = 4.3 Hz, OH), 1.83 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.70 (3 H, dm, *J* = 6.3 Hz, H4′), 1.76, 1.48, 1.10 (4 H, m, H5, H6), 1.00 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 0.78 (3 H, s, CH_3). Anal. Calcd for $C_{14}H_{24}OS$: C, 70.0; H, 10.1. Found: C, 69.8; H, 9.7.

(1*R*,2*S*)-*exo*-3-[(3′-Methylbut-2′-enyl)thio]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (24). The crude product obtained from the *exo*-3-[(dimethylallyl)thio]camphor **10** (530 mg, 2.1 mmol) and diisobutylaluminum hydride (3.2 mmol) was submitted to chromatography with 3:97 ether:light petroleum ether and distilled to give the product **24** as a colorless oil (390 mg, 73%), bp 220–230 °C (0.7 mm), $[\alpha]_D$ −1.1° (*c* 2.0, acetone): ^{1}H NMR δ 5.23 (1 H, tm, *J* = 7.8 Hz, H2′), 3.54 (1 H, dd, $J_{2,3}$ = 7.5, $J_{2,OH}$ = 4.2 Hz, H2), 3.12 (2 H, dm, *J* = 7.8 Hz, H1′), 2.98 (1 H, d, $J_{OH,2}$ = 4.2 Hz, OH), 2.94 (1 H, d, $J_{3,2}$ = 7.5 Hz, H3), 1.82 (1 H, d, $J_{4,5exo}$ = 5.4 Hz, H4), 1.75 (3 H, s, CH_3), 1.67 (3 H, s, CH_3), 1.78, 1.48, 1.09 (4 H, m, H5, H6), 0.99 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 0.78 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{24}OS$: C, 70.8; H, 10.3. Found: C, 70.7; H, 10.0.

(1*R*,2*S*,2′*E*)-*exo*-3-(Oct-2′-enylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (25). The crude product obtained from the *exo*-3-(octenylthio)camphor **11** (620 mg, 2.1 mmol) and diisobutylaluminum hydride (3.3 mmol) was purified by chromatography with 3:97 ether:light petroleum ether and distilled to give the product **25** as a colorless oil (380 mg, 61%), bp 250° (0.5 mm), $[\alpha]_D$ +5.6° (*c* 2.0, acetone): ^{1}H NMR δ 5.54 (1 H, m, H2′), 5.40 (1 H, m, H3′), 3.52 (1 H, dd, $J_{2,3}$ = 7.5, $J_{2,OH}$ = 4.1 Hz, H2), 3.06 (2 H, m, H1′), 2.93 (1 H, d, $J_{3,2}$ = 7.5 Hz, H3), 2.91 (1 H, d, $J_{OH,2}$ = 4.1 Hz, OH), 2.03 (2 H, m, H4′), 1.82 (1 H, d, $J_{4,5exo}$ = 4.0 Hz, H4), 1.77, 1.48, 1.41–1.22, 1.09 (10 H, m, H5, H6, H5′, H6′, H7′), 0.89 (3 H, t, *J* = 6.9 Hz, H8′), 1.00 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 0.77 (3 H, s, CH_3). Anal. Calcd for $C_{18}H_{32}OS$: C, 72.9; H, 10.9 Found: C, 72.7; H, 10.7.

(1*R*,2*S*)-*exo*-3-(Methylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (26). The crude product obtained from the *exo*-3-(methylthio)camphor **12** (450 mg, 2.3 mmol) and diisobutylaluminum hydride (3.5 mmol) was purified by chromatography with 3:97 ether:light petroleum ether and distilled to give the product **26** as a colorless oil (310 mg, 68%), bp 145 °C (1 mm), $[\alpha]_D$ +7.6° (*c* 2.0, acetone): ^{1}H NMR δ 3.63 (1 H, dd, $J_{2,3}$ = 7.6, $J_{2,OH}$ = 5.0 Hz, H2), 2.98 (1 H, d, $J_{OH,2}$ = 5.0 Hz, OH), 2.92 (1 H, d, $J_{3,2}$ = 7.6 Hz, H3), 2.11 (3 H, s, SCH_3), 1.87 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 1.78, 1.49, 1.11 (4 H, m, H5, H6), 1.01 (3 H, s, CH_3), 0.97 (3 H, s, CH_3), 0.78 (3 H, s, CH_3). Anal. Calcd for $C_{11}H_{20}OS$: C, 66.0; H, 10.1. Found: C, 65.8; H, 9.9.

(1*R*,2*S*)-*exo*-3-(Propylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (27). The crude product obtained from the *exo*-3-(propylthio)camphor **13** (440 mg, 2.0 mmol) and diisobutylaluminum hydride (2.5 mmol) was submitted to chromatography with 3.5:96.5 ether:light petroleum ether and distilled to give the product **27** as a colorless oil (270 mg, 67%), bp 190–195 °C (1 mm), $[\alpha]_D$ +3.7° (*c* 2.0, acetone): ^{1}H NMR δ 3.57 (1 H, dd, $J_{2,3}$ = 7.7, $J_{2,OH}$ = 4.4 Hz, H2), 3.06 (1 H, d, $J_{OH,2}$ = 4.4 Hz, OH), 2.94 (1 H, d, $J_{3,2}$ = 7.7 Hz, H3), 2.47 (2 H, m, H1′), 1.87 (1 H, d, $J_{4,5exo}$ = 4.2 Hz, H4), 1.78, 1.49, 1.11 (4 H, m, H5, H6), 1.61 (2 H, m, H2′), 0.99 (3 H, t, *J* = 7.5 Hz, H3′), 0.99 (3 H, s, CH_3), 0.97 (3 H, s, CH_3), 0.78 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{24}OS$: C, 68.4; H, 10.6. Found: C, 68.1; H, 10.5.

(1*R*,2*S*)-*exo*-3-(Benzylthio)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (28). The crude product obtained from the *exo*-3-(benzylthio)camphor **14** (680 mg, 2.5 mmol) and diisobutylaluminum hydride (3.5 mmol) was submitted to chromatography with 3.5:96.5 ether:light petroleum ether and distilled to give the product **28** as a colorless oil (580 mg, 85%), bp 250 °C (0.7 mm), $[\alpha]_D$ −8.9° (*c* 3.0, acetone): ^{1}H NMR δ 7.30 (5 H, m, C_6H_5), 3.70 (2 H, s, H1′), 3.47 (1 H, dd, $J_{2,3}$ = 7.5, $J_{2,OH}$ = 4.3 Hz, H2), 2.94 (1 H, d, $J_{3,2}$ = 7.5 Hz, H3), 2.67 (1 H, d, $J_{OH,2}$ = 4.3 Hz, OH), 1.79 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.72, 1.45, 1.05 (4 H,

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m, H5, H6), 0.99 (3 H, s, CH_3), 0.93 (3 H, s, CH_3), 0.75 (3 H, s, CH_3). Anal. Calcd for $C_{17}H_{24}OS$: C, 73.9; H, 8.8. Found: C, 74.0; H, 8.6.

Preparation of 3-*exo*-(Allylsulfinyl)isoborneols and 3-*exo*-(Alkylsulfinyl)isoborneols 31–37. (1*R*,2*S*,*S*$_S$)-3-*exo*-(Prop-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (31). *m*-Chloroperbenzoic acid (193 mg, 1.12 mmol) in THF (5 mL) was added to a solution of the *exo*-(allylthio)isoborneol **22** (230 mg, 1.02 mmol) in THF (15 mL) at −78 °C under nitrogen over a period of 5 min. The resulting mixture was stirred at this temperature for 30 min. The cold solution was poured onto an aqueous sodium sulfide solution (20%, 75 mL) and extracted into ether (3 × 30 mL). The combined ether extracts were washed with saturated aqueous sodium hydrogen carbonate solution (2 × 50 mL) and dried ($MgSO_4$). The solvent was removed and the product was recrystallized from ether to give colorless fine needles of the product **31** (148 mg, 60%), mp 133–135 °C, $[\alpha]_D$ +32° (*c* 0.88, acetone): ^{1}H NMR δ 6.01 (1 H, m, H2′), 5.40 (2 H, m, H3′), 4.09 (1 H, dd, $J_{2,3}$ = 7.2, $J_{2,OH}$ = 3.5 Hz, H2), 3.72 (1 H, d, $J_{OH,2}$ = 3.5 Hz, OH), 3.65 (1 H, ddm, J = 13.6, J = 6.8 Hz, H1′), 3.29 (1 H, ddm, J = 13.6, J = 8.0 Hz, H1′), 3.06 (1 H, d, $J_{3,2}$ = 7.2 Hz, H3), 1.81 (1 H, m, H5exo), 1.70 (1 H, d, $J_{4,5exo}$ = 4.5 Hz, H4), 1.54 (1 H, m, H6exo), 1.10 (2 H, m, H5endo, H6endo), 1.23 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.83 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.4; H, 9.2. Found: C, 64.3; H, 9.3.

(1*R*,2*S*,2′*E*,*S*$_S$)-*exo*-3-(But-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (32). The crude product obtained from the (butenylthio)isoborneol **23** (290 mg, 1.21 mmol) and *m*-chloroperbenzoic acid (270 mg, 1.57 mmol) was submitted to chromatography with ethyl acetate followed by 5:95 ethanol:ethyl acetate and the solvent removed at room temperature to yield the product **32** as colorless crystals (235 mg, 76%), mp 91–93 °C, $[\alpha]_D$ +9.4° (*c* 2.0, acetone): ^{1}H NMR δ 5.94 (1 H, m, H2′), 5.51 (1 H, m, H3′), 4.10 (1 H, dd, $J_{2,3}$ = 7.3, $J_{2,OH}$ = 3.3 Hz, H2), 3.69 (1 H, d, $J_{OH,2}$ = 3.3 Hz, OH), 3.58 (1 H, ddm, J = 13.5, J = 6.5 Hz, H1′), 3.23 (1 H, ddm, J = 13.5, J = 8.0 Hz, H1′), 3.04 (1 H, d, $J_{3,2}$ = 7.3 Hz, H3), 1.80 (3 H, dm, J = 6.0 Hz, H4′), 1.68 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.83, 1.55, 1.10 (4 H, m, H5, H6), 1.24 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.77 (3 H, s, CH_3); HRMS calcd for $C_{14}H_{24}O_2S$ 256.1497, found 256.1499.

(1*R*,2*S*,*S*$_S$)-*exo*-3-[(3′-Methylbut-2′-enyl)sulfinyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (33). The crude product obtained from the [(dimethylallyl)thio]isoborneol **24** (280 mg, 1.10 mmol) and *m*-chloroperbenzoic acid (240 mg, 1.40 mmol) was submitted to chromatography with ethyl acetate followed by 5:95 ethanol:ethyl acetate and the solvent was removed at room temperature to leave the product **33** as colorless needles (190 mg, 64%), mp 84–86 °C, $[\alpha]_D$ +32° (*c* 1.0, dichloromethane): ^{1}H NMR δ 5.39 (1 H, ddm, J = 8.5, J = 7.0 Hz, H2′), 4.11 (1 H, dd, $J_{2,3}$ = 7.3, $J_{2,OH}$ = 2.8 Hz, H2), 3.62 (1 H, br s, OH), 3.60 (1 H, dd, J = 13.5, J = 7.0 Hz, H1′), 3.33 (1 H, dd, J = 13.5, J = 8.5 Hz, H1′), 3.06 (1 H, d, $J_{3,2}$ = 7.3 Hz, H3), 1.87 (3 H, s, CH_3), 1.73 (3 H, s, CH_3), 1.67 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.81, 1.56, 1.10 (4 H, m, H5, H6), 1.25 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.84 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{26}O_2S$: C, 66.6; H, 9.7. Found: C, 66.8; H, 10.0.

(1*R*,2*S*,2′*E*,*S*$_S$)-*exo*-3-(Oct-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (34). The crude product obtained from the (octenylthio)isoborneol **25** (350 mg, 1.18 mmol) and *m*-chloroperbenzoic acid (240 mg, 1.40 mmol) was submitted to chromatography with ethyl acetate followed by 5:95 ethanol:ethyl acetate and the solvent was removed at room temperature to yield the product **34** as colorless crystals (300 mg, 81%), mp 82–84 °C, $[\alpha]_D$ +11.4° (*c* 2.0, acetone): ^{1}H NMR δ 5.78 (2 H, m, H2′), 5.61 (1 H, m, H2′), 4.09 (1 H, dd, $J_{2,3}$ = 7.3, $J_{2,OH}$ = 3.3 Hz, H2), 3.67 (1 H, d, $J_{OH,2}$ = 3.3 Hz, OH), 3.60 (1 H, ddm, J = 13.5, J = 6.5 Hz, H1′), 3.23 (1 H, dd, J = 13.5, J = 8.3 Hz, H1′), 2.12 (2 H, dt, J = 7.3, J = 7.0 Hz, H4′), 1.72 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.82, 1.55, 1.41, 1.30, 1.09 (10 H, m, H5, H6, H5′, H6′, H7′), 1.24 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.83 (3 H, s, CH_3), 0.87 (3 H, t, J = 7.0 Hz, H8′). Anal. Calcd for $C_{18}H_{32}O_2S$: C, 69.9; H, 10.3. Found: C, 70.3; H, 10.2.

(1*R*,2*S*,*S*$_S$)-*exo*-3-(Methylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (35). The crude product obtained from the (methylthio)isoborneol **26** (230 mg, 1.15 mmol) and *m*-chloroperbenzoic acid (230 mg, 1.34 mmol) was submitted to chromatography with ethyl acetate and 5:95 ethanol:ethyl acetate and recrystallized from light petroleum ether to give the product **35** as colorless needles (166 mg, 67%), mp 147–148 °C, $[\alpha]_D$ +62° (*c* 3.0, acetone): ^{1}H NMR δ 4.20 (1 H, d, $J_{OH,2}$ = 4.4 Hz, OH), 4.09 (1 H, dd, $J_{2,3}$ = 7.2, $J_{2,OH}$ = 4.4 Hz, H2), 2.95 (2 H, d, $J_{3,2}$ = 7.2 Hz, H3), 2.60 (3 H, s, CH_3), 1.69 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.84, 1.54, 1.14 (4 H, m, H5, H6), 1.19 (3 H, s, CH_3), 0.99 (3 H, s, CH_3), 0.82 (3 H, s, CH_3). Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.1; H, 9.3. Found: C, 61.4; H, 9.0.

(1*R*,2*S*,*S*$_S$)-*exo*-3-(Propylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (36). The crude product obtained from the 3-(propylthio)isoborneol **27** (230 mg, 1.01 mmol) and *m*-chloroperbenzoic acid (230 mg, 1.34 mmol) was submitted to chromatography with ethyl acetate then 5:95 ethanol:ethyl acetate and recrystallized from light petroleum ether to give the product **36** as colorless needles (180 mg, 73%), mp 142–144 °C, $[\alpha]_D$ −6.9° (*c* 4.0, acetone): ^{1}H NMR δ 4.10, dd, $J_{2,3}$ = 7.0, $J_{2,OH}$ = 3.6 Hz, H2), 4.05 (1 H, d, $J_{OH,2}$ = 3.6 Hz, OH), 2.97 (1 H, d, $J_{3,2}$ = 7.0 Hz, H3), 2.73 (1 H, m, H1′), 2.63 (1 H, m, H1′), 1.70 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.85, 1.55, 1.13 (6 H, m, H5, H6, H2′), 1.10 (3 H, t, J = 7.4 Hz, H3′), 1.22 (3 H, s, CH_3), 0.99 (3 H, s, CH_3), 0.83 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{24}O_2S$: C, 63.9; H, 9.9. Found: C, 64.3; H, 9.8.

(1*R*,2*S*,*S*$_S$)-*exo*-3-(Benzylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (37). The crude product obtained from the (benzylthio)isoborneol **28** (490 mg, 1.78 mmol) and *m*-chloroperbenzoic acid (380 mg, 2.21 mmol) was submitted to chromatography with ethyl acetate followed by 5:95 ethanol:ethyl acetate and recrystallized from light petroleum ether to give the product **37** as colorless needles (460 mg, 89%), mp 127–128 °C, $[\alpha]_D$ −53° (*c* 1.0, acetone): ^{1}H NMR δ 7.42–7.28 (5 H, m, C_6H_5), 4.14 (1 H, d, J = 13.5 Hz, H1′), 3.83 (1 H, d, J = 13.5 Hz, H1′), 4.00, (1 H, dd, $J_{2,3}$ = 7.0, $J_{2,OH}$ = 2.5 Hz, H2), 3.44 (1 H, d, $J_{OH,2}$ = 2.5 Hz, OH), 2.78 (1 H, d, $J_{3,2}$ = 7.0 Hz, H3), 1.68 (1 H, d, $J_{4,5exo}$ = 4.2 Hz, H4), 1.80, 1.52, 1.01 (4 H, m, H5, H6), 1.27 (3 H, s, CH_3), 0.97 (3 H, s, CH_3), 0.84 (3 H, s, CH_3). Anal. Calcd for $C_{17}H_{24}O_2S$: C, 69.8; H, 8.3. Found: C, 70.1; H, 8.0.

Preparation of Sulfoxides 38 and 39. (1*R*)-*endo*-3-(Methylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one (38). A solution of sodium metaperiodate (610 mg, 2.85 mmol) in water (2 mL) was added dropwise to a solution of the *endo*-3-(methylthio)camphor **19** (506 mg, 2.56 mmol) in methanol (10 mL) at 0 °C. Upon completion of the addition the reaction mixture was then stirred at room temperature for 12 h. The reaction mixture was poured into water (20 mL) and extracted into ether (3 × 30 mL), the combined ether extracts were dried ($MgSO_4$), and the solvent was evaporated to leave a yellow oil. This was submitted to medium pressure liquid chromatography with 1:1 ethyl acetate:light petroleum ether to give a mixture of diastereomers of the product **38** as a yellow oil (490 mg, 90%). Analysis of the mixture by reverse-phase HPLC with 60:40 methanol:water indicated the ratio of the more polar to the less polar diastereomer was 78:22. The less polar component was thereby obtained as a colorless oil, $[\alpha]_D$ −67.5° (*c* 1.0, acetone): ^{1}H NMR δ 3.27 (1 H, dd, $J_{3,4}$ = 4.4, $J_{3,5exo}$ = 2.4 Hz, H3), 2.90 (3 H, s, CH_3), 2.44 (1 H, dd, $J_{4,3}$ = 4.4, $J_{4,5exo}$ = 4.2 Hz, H4), 2.08, 1.90, 1.71 (4 H, m, H5, H6), 1.04 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 0.90 (3 H, s, CH_3); HRMS calcd for $C_{11}H_{18}O_2S$ 214.1027, found 214.1019.

The more polar component was a colorless oil, $[\alpha]_D$ +100.9° (*c* 1.0, acetone): ^{1}H NMR δ 3.63 (1 H, dd, $J_{3,4}$ = 4.3, $J_{3,5exo}$ = 2.0 Hz, H3), 2.92 (3 H, s, CH_3), 2.64 (1 H, dd, $J_{4,3}$ = 4.3, $J_{4,5exo}$ = 4.2 Hz, H4), 2.12, 2.02, 1.83, 1.44 (4 H, m, H5, H6), 1.08 (3 H, s, CH_3), 0.96 (3 H, s, CH_3), 0.93 (3 H, s, CH_3); HRMS calcd for $C_{11}H_{18}O_2S$ 214.1027, found 214.1036.

Use of *m*-chloroperbenzoic acid in dichloromethane gave the diastereomers of sulfoxide **38** in a ratio of the more polar:less polar of 59:41.

(1*R*)-*exo*-3-(Prop-2′-enylsulfinyl)-1,7,7-trimethylbicyclo-[2.2.1]heptan-2-one (39). The crude product obtained from the (allylthio)camphor **8** (250 mg, 1.12 mmol) and *m*-chloroperbenzoic acid (240 mg, 1.40 mmol) was purified by chromatography with ethyl acetate followed by 5:95 ethanol:ethyl acetate to give the product **39** as a colorless oil (190 mg, 71%), $[\alpha]_D$ +96° (*c* 1.0, acetone). ^{1}H NMR analysis indicated this sample contained >95% of one diastereomer: ^{1}H NMR (major isomer) δ 5.87 (1 H, dddd, J = 17.0, J = 10.3, J = 8.5, J = 6.3 Hz, H2′), 5.52 (1 H, dm, J

= 10.3 Hz, H3′), 5.45 (1 H, dm, J = 17.0 Hz, H3′), 3.98 (1 H, ddm, J = 13.5, J = 6.3, H1′), 3.56 (1 H, ddm, J = 13.5, J = 8.5 Hz, H1′), 3.34 (1 H, s, H3), 2.70 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 2.18, 1.75, 1.50 (4 H, m, H5, H6), 1.03 (3 H, s, CH_3), 1.00 (3 H, s, CH_3), 0.94 (3 H, s, CH_3); ^{1}H NMR (minor isomer) δ 3.09 (1 H, s, H3); HRMS calcd for $C_{13}H_{20}O_2S$ 240.1184, found 240.1174.

Epimerization of the 3-*exo*-(Allylsulfinyl)isoborneols 31–34. (1*R*,2*S*,*R*$_S$)-*exo*-3-(Prop-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (41). A melt of the S_S sulfoxide **31** (200 mg, 0.83 mmol) was heated at 140 °C for 1 h in a stoppered tube. The R_S sulfoxide **41** slowly crystallized out of the melt at this temperature. The reaction was followed by HPLC (1:99 ethanol:ethyl acetate, Brownlee SI 100, 4.6 mm i.e. × 25 cm 5-μm column at 600 psi, S_S sulfoxide, t_R 18 min, R_S sulfoxide, t_R 14.8 min). After epimerization was complete, the product was recrystallized from ethyl acetate/light petroleum ether to give the product (190 mg, 95%) as colorless cubes, mp 171–174 °C, $[\alpha]_D$ +92° (c 0.85, acetone): ^{1}H NMR δ 6.04 (1 H, m, H2′), 5.42 (2 H, m, H3′), 3.89 (1 H, ddm, J = 13.1, J = 6.7 Hz, H1′), 3.46 (1 H, ddm, J = 13.1, J = 8.5 Hz, H1′), 3.84 (1 H, dd, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.8 Hz, H2), 3.02 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.68 (1 H, d, $J_{OH,2}$ = 4.8 Hz, OH), 2.38 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 1.90, 1.57, 1.08 (4 H, m, H5, H6), 1.31 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.4; H, 9.2. Found: C, 64.6; H, 9.2.

(1*R*,2*S*,2′*E*,*R*$_S$)-*exo*-3-(But-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (42). A melt of the S_S sulfoxide **32** was heated at 110 °C for 20 min. After this time complete crystallization of the sample was observed. The colorless needles of the product **42** so obtained (>95%) had the following: mp 175–177 °C, $[\alpha]_D$ +108° (c 1.0, acetone); ^{1}H NMR δ 5.83 (1 H, dqm, J = 15.3, J = 6.5 Hz, H3′), 5.66 (1 H, dtm, J = 15.3, J = 7.5 Hz, H2′), 3.83 (1 H, dd, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.8 Hz, H2), 3.84 (1 H, m, H1′), 3.35 (1 H, dd, J = 13.0, J = 8.0 Hz, H1′), 3.20 (1 H, m, OH), 2.98 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.36 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.78 (3 H, dm, J = 6.5 Hz, H4′), 1.88, 1.70, 1.56, 1.07 (4 H, m, H5, H6), 1.30 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.6; H, 9.4. Found: C, 65.7; H, 9.2.

(1*R*,2*S*,*R*$_S$)-*exo*-3-[(3′-Methylbut-2′-enyl)sulfinyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (43). A melt of the S_S sulfoxide **33** was heated at 90° for 20 min or until complete crystallization had taken place to give colorless needles (>95%), mp 199–200 °C of the product **43**, $[\alpha]_D$ +127° (c 1.0, dichloromethane): ^{1}H NMR δ 5.45 (1 H, ddm, J = 8.3, J = 7.5 Hz, H2′), 3.88 (1 H, dd, J = 13.3, J = 7.5 Hz, H1′), 3.40 (1 H, dd, J = 13.3, J = 8.3 Hz, H1′), 3.86 (1 H, $J_{2,3}$ = 7.8, $J_{2,OH}$ = 4.5 Hz, H2), 3.01 (1 H, d, $J_{3,2}$ = 7.8 Hz, H3), 2.65 (1 H, d, $J_{OH,2}$ = 4.5 Hz, OH), 2.32 (1 H, d, $J_{4,5exo}$ = 4.3 Hz, H4), 1.83 (3 H, s, CH_3), 1.74 (3 H, s, CH_3), 1.89, 1.57, 1.08 (4 H, m, H5, H6), 1.37 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3). Anal. Calcd for $C_{15}H_{26}O_2S$: C, 66.6; H, 9.7. Found: C, 66.6; H, 9.4.

(1*R*,2*S*,2′*E*,*R*$_S$)-*exo*-3-(Oct-2′-enylsulfinyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (44). The S_S sulfoxide **34** was heated at 110 °C for 2 h. The colorless oil so obtained was shown by ^{1}H NMR spectroscopy to consist of the R_S and S_S diastereomers **44** and **34** in a ratio of 9:1. Separation of this mixture could not be achieved and hence the substance was analyzed as a mixture, which had $[\alpha]_D$ +60° (c 2.0, acetone): ^{1}H NMR [R_S epimer] δ 5.82 (1 H, m, H2′), 5.66 (1 H, m, H3′), 3.84 (1 H, m, H1′), 3.39 (1 H, dd, J = 12.8, J = 8.0 Hz, Hu′), 3.82 (1 H, dd, $J_{2,3}$ = 7.6, $J_{2,OH}$ = 5.2 Hz, H2), 3.02 (1 H, d, $J_{3,2}$ = 7.6 Hz, H3), 2.39 (1 H, d, $J_{4,5exo}$ = 4.4 Hz, H4), 2.31 (1 H, d, $J_{OH,2}$ = 5.2 Hz, OH), 2.13 (2 H, dt, J = 7.2, J = 6.4 Hz, H4′), 1.89, 1.57, 1.38, 1.26, 1.06 (10 H, m, H5, H6, H5′, H6′, H7′), 1.31 (3 H, s, CH_3), 0.94 (3 H, s, CH_3), 0.87 (3 H, s, CH_3), 0.89 (3 H, t, J = 6.5 Hz, H8′); HRMS calcd for $C_{18}H_{31}OS$ 295.2096, found 295.2092.

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Supplementary Material Available: Characterization data, including IR, UV, $[\alpha]_D$, and mass spectral data for compounds **2–4**, **8–18**, **20–28**, **31–39**, and **41–44**; crystallographic data for **31** (14 pages). Ordering information is given on any current masthead page.

Cross-Conjugated and Pseudo-Cross-Conjugated Mesomeric Betaines. 1. Synthesis and Characterization†

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Reaction of pyrazoles, 1,2,3-triazoles, and 1,2,4-triazoles with aryl(chlorocarbonyl)ketenes, alkylmalonyl dichlorides, or carbon suboxide results in a series of cross-conjugated mesomeric betaines, characterized by the presence of distinct cationic and anionic segments. 1-Substituted imidazoles, suitably substituted 1,2,4-triazoles, and pyridine with the above reagents give rise to pseudo-cross-conjugated mesomeric betaines which, in addition to charge separation, are characterized by the presence of the 2-oxyallyl cation 1,3-dipole. Alternative syntheses of cross-conjugated mesomeric betaines which allow the introduction of more diverse substituents are also described.

Introduction

In a recent review of the chemistry of heterocyclic, mesomeric betaines (MB), Ollis, Stanforth, and Ramsden contrast[2a] the characteristics of conjugated mesomeric betaines (CMB), cross-conjugated mesomeric betaines (CCMB), and pseudo-cross-conjugated mesomeric betaines (PCCMB) and detail the known and potential dipolar cycloaddition characteristics of each family of mesomeric betaine. Although representatives of CMB are well-known, e.g., mesoionic compounds, pyridinium ylides, etc., only a few scattered reports of heterocycles that may be classified as CCMB or PCCMB have appeared. In our con-

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