thio)but-2-ene, 107183-91-5; 1-(phenylthio)-3-methylbut-2-ene, 13640-71-6; 1-bromo-3-methylbut-2-ene, 870-63-3; 1-(1,1-dimethylethyl)-3-methylbut-2-ene, 114678-54-5; 3-(phenylthio)pent-4-en-1-ol, 114678-56-7; 5-(phenylthio)pent-3-en-1-ol, 114678-57-8; *tert*-butyldimethylsilyl chloride, 18162-48-6; 5-(phenylthio)pent-3-en-1-ol *tert*-butyldimethylsilyl ether, 114678-60-3; oct-1-en-3-ol, 3391-86-4; chlorodiphenylphosphine, 1079-66-9; (*E*)-1-bromooct-2-ene, 53645-21-9; (*Z*)-1-bromooct-2-ene, 56318-83-3; but-3-en-2-ol, 598-32-3; triethyl phosphite, 122-52-1; diethyl phosphite, 762-04-9; tributylphosphine, 998-40-3.

Supplementary Material Available: Commentary on determination of relative configuration and preferred conformers of compounds **25**, **26**, **30**, and **31**, with figure, and table of ^{1}H NMR data for compounds **25**, **26**, **53**, and **54** (5 pages). Ordering information is given on any current masthead page.

Aprotic Conjugate Addition of Allyllithium Reagents Bearing Polar Groups to Cyclic Enones. 2. 2-Alkyl-, 2,3-Dialkyl-, and 1,3-Dialkylallyl Systems

Richard K. Haynes,*,† Andrew G. Katsifis,† Simone C. Vonwiller,† and Trevor W. Hambley‡

Contribution from the Departments of Organic Chemistry and Inorganic Chemistry, The University of Sydney, Sydney, 2006, New South Wales, Australia. *Received September 11, 1987*

Abstract: As an extension of the work carried out on the conjugate addition reactions of lithiated 3-alkylallylic sulfoxides, phosphine oxides, and phosphonates to cyclic enones, the effects of placing methyl groups at C2, at C2 and C3, and at C1 and C3 of the allyl system and of placing the allyl system within a five-membered ring are examined. From the lithiated 2-methallyl and (*E*)-2-methylbut-2-enyl ("tiglyl") sulfoxides, mixtures of diastereomeric (*E*)- and (*Z*)-vinylic sulfoxides resulting from conjugate addition to cyclopentenone are obtained. The proportion of *Z* diastereomers formed increases with the reaction temperature. In contrast, lithiated (*Z*)-2-methylbut-2-enyl ("angelyl") sulfoxides and the tiglyl and angelyl phosphine oxides undergo highly diastereoselective conjugate addition to give (*E*)-vinylic products. Lithiated 1,3-dimethylbut-2-enyl sulfoxides undergo stereoconvergent reactions in that the starting sulfoxides, as mixtures of diastereomers, are converted into vinylic sulfoxides, which are obtained as single diastereomers. The individual diastereomers of *tert*-butyl cyclopentenyl sulfoxide upon lithiation undergo conjugate addition with cyclopentenone to give the same vinylic sulfoxide. A sulfenate ester also results from carbonyl addition. The structures of the diastereomers have been established by high-field ^{1}H NMR spectroscopy, by chemical correlation, and in two cases by X-ray crystallographic studies. The destabilizing influence of the methyl groups on the normal "trans-fused chair–chair"-like extended transition state causing access to "cis-fused boat–boat"-like, "cis-fused chair–chair"-like, and "trans-fused boat–chair"-like transition states involving planar lithiated reagents provides a rationale for the results. The temperature dependence of some of these reactions, and simple quenching experiments in which the individual lithiated diastereomers of the cyclopentenyl sulfoxide are converted into a single diastereomer, provide evidence for planar lithiated sulfoxides.

In the preceding paper, we described how lithiated (*E*)- and (*Z*)-allylic sulfoxides, phosphine oxides, and phosphonates bearing alkyl groups at C3 undergo highly stereoselective aprotic conjugate addition to cyclic enones to give *syn*- and *anti*-vinylic sulfoxides, phosphine oxides, and phosphonates. We proposed an extended transition-state model of the reactions that is described as "trans-decalyl"- or "trans-fused chair–chair"-like.[1] The model has the advantage that it is conceptually simple, easily visualized, and consistently accounts for the regiochemical and stereochemical features of the reactions of the foregoing substrates. Central to the proposition is the assumption that the lithiated reagents are planar, with the lithium bound to the oxygen atom.[1]

A natural extension of the work is to examine allylic systems more encumbered than those described hitherto. It is of synthetic benefit to establish how tolerant these reactions are of substitution at C1 and C2 in the allylic system and to delineate the steric limitations of these reactions in general. Further, the effect of such substitution will provide a test of the validity of the extended TS model. If this is a reasonable representation of the TS, then the reaction should be sensitive to the presence of substituents, attached to either the allyl system or the cyclic enone, that engender steric interactions between the reactants in the TS. The interactions may be such that either other extended transition states become energetically accessible to the reactants or, alternatively, flowover into the carbonyl addition manifold takes place.[2] For conjugate addition, the intercession of other extended transition states will reflect in the formation of vinylic products that possess configurations different from those of the syn and anti products described above.

We chose to investigate the reactions of the lithiated reagents derived from 2-methallyl sulfoxides **1** and **2**, (*E*)- ("tiglyl") and (*Z*)-2-methylbut-2-enyl ("angelyl") sulfoxides **3** and **4**, and phosphine oxides **5** and **6**, all of which possess a 2-methyl group capable of destabilizing a trans-fused chair–chair-like TS (cf. Figure 1). Also considered were the sulfoxides **7** and **8**, as 1,3-disubstitution is also anticipated to influence the manner in which the lithiated reagents react. These compounds, however, are of particular interest in that they possess a stereogenic center at C1, and thus the outcome of the reactions of the individual lithiated diastereomers of each should provide insight into the structures of the lithiated reagents in general. This applies also to the cyclopentenyl sulfoxide **9**. In addition, the allyl systems within both compound **9** and the phosphine oxide **10** are constrained to react so as to generate (*E*)-vinylic sulfoxides and

† Department of Organic Chemistry.
‡ Department of Inorganic Chemistry.

(1) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C., preceding paper in this issue.
(2) This has already been noted in reactions involving lithiated 3,3-dimethallyl sulfoxides and 3-methylcyclopent-2-enone.[1]

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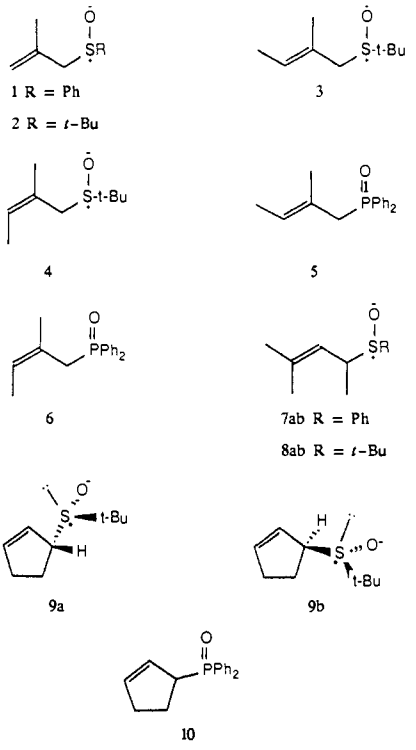
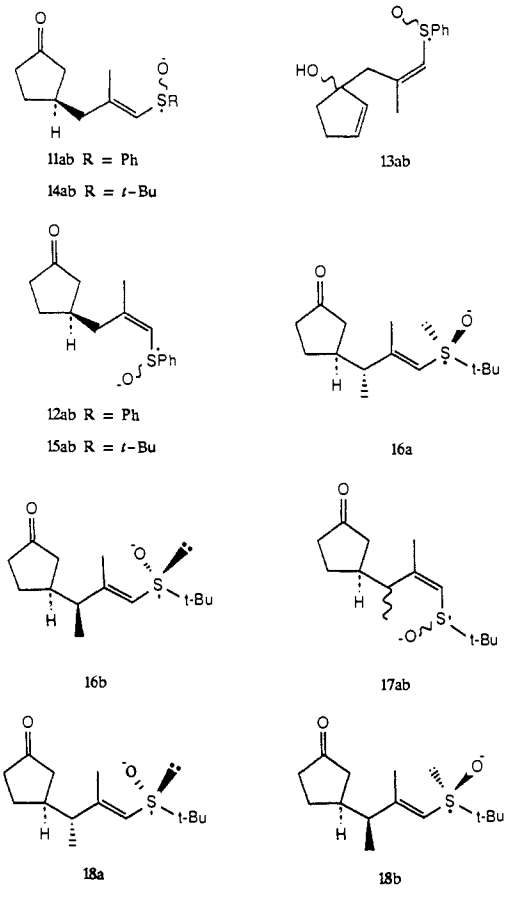


phosphine oxides, and thus a comparison of the reactivities of the lithiated compounds with those of the 1,3-disubstituted, acyclic counterparts, where no such constraint exists, can be made.

Results and Discussion

2-Alkyl and 2,3-Dialkyl Sulfoxides and Phosphine Oxides. From lithiated 2-methallyl phenyl sulfoxide (**1**) and cyclopent-2-enone in THF at −70 °C are obtained the vinylic sulfoxides **11a,b**[3] arising from "normal" conjugate addition and **13a,b** arising from carbonyl addition. That the conjugate adducts possess an *E* and the carbonyl adducts a *Z* double bond was verified by NOE experiments involving preirradiation of the vinylic protons in each pair of diastereomers.[4] The carbonyl adducts **13a,b** are not obtained from reactions initially conducted at −70 °C and quenched at −10 °C. The lithium alkoxides of these adducts generated at −70 °C dissociate to the sulfoxide **1** (40%) and undergo dissociation–recombination to give equal amounts of the conjugate adducts **11a,b** and **12a,b** (40%) at −10 °C; unchanged carbonyl adducts **13a,b** (20%) are also recovered in this experiment. The yields of each product obtained from the lithiated sulfoxide **1** and the conditions for their formation are given in Table I. The lithiated *tert*-butyl sulfoxide **2** on the other hand undergoes exclusive conjugate addition to cyclopent-2-enone to give the products **14a,b** and **15a,b** (Table I). It is noteworthy that the relative amount of the (*Z*)-vinylic sulfoxides **15a,b** formed increases markedly with temperature.



(3) Diastereomers are designated by **a** and **b**.

Table I. Yields of Products **11–18** from Sulfoxides **1–4**

sulfoxide	temp,[a] °C	products (**a**:**b**)[b]		*E*:*Z* ratio	overall yield,[c] %
1	−70, −70, −70	**11** (1:1)	**13** (52:48)	82:18	69
1	−70, −10, −10	**11** (1:1)	**12** (75:25)	74:26	93
1	−70, −70, −10	**11**	**12**		
2	−70, −70, −70	**14** (59:41)	**15** (1:1)	94:6	68
2	−15, −10, −10	**14** (58:42)	**15** (77:23)	66:34	73
2	−70, −70, −10	**14**	**15**	73:27	83
3	−70, −70, −70	**16** (66:34)	**17** (66:34)	84:16	84
3	−70, −10, −10	**16** (53:47)	**17** (67:33)	71:28	66
4	−70, −70, −70	**18** (93:7)			61

[a] Temperature of lithiation of sulfoxide, temperature of addition of enone, temperature of quench. [b] Diasteromer ratios (**a**:**b**) as determined by 400-MHz ^{1}H NMR spectroscopy are given in parentheses. [c] Overall yields have not been adjusted to take account of variable amounts of starting sulfoxides also isolated from the reaction mixtures.

Thus, the reactions of the 2-methallyl sulfoxides, in terms of their regiochemical outcome, diastereoselectivity and temperature dependence differ remarkably from the reactions of the lithiated 3-alkylallyl sulfoxides. The results of Table I indicate that the sulfoxides are lithiated to give *equilibrating transoid* and *cisoid* carbanions, which react through *four* different extended transition states with cyclopentenone. In *only* the first case, flowover of the reactions into the carbonyl addition manifold takes place to give the sulfoxides **13a,b**, which obviously arise from the cisoid carbanion. The isolation of the *E*- and *Z*-conjugate adducts **11a,b** and **12a,b** from the (*Z*)-carbonyl adducts **13a,b** strongly supports the idea of equilibrating ions. Although we have not been able to separate the diastereomers **a** and **b** of the conjugate addition products **11a,b**, or establish relative configurations of **11a,b** and **12a,b**, the formation of all possible diastereomers can be readily explained by invoking each of the extended transition states that are seemingly accessible to the lithiated sulfoxides. These are depicted in Figure 1 for the reactions of the sulfoxide **2**, in which the "cis-fused boat–boat"-like transition state T2 involving the transoid carbanion, and the "cis-fused chair–chair"-like and "cis-fused boat–chair"-like transition states T3 and T4 involving the cisoid carbanion are now rendered accessible through the methyl group at C2 of the allylic system destabilizing the trans-fused chair–chair-like TS T1.[5] In all cases, the *tert*-butyl group is pseudoequatorial, the sulfoxide lone pair pseudoaxial. The carbanion lies over one face of the enone, adopting either an

(4) Preirradiation of H3′ (at δ 6.6 in **11a,b**, δ 6.17 in **12a,b**) induced enhancement (4.5%) of both signals due to H1′ (at δ 2.28) in **11a,b** and enhancement (5.6%, 3%) of the methyl signals (at δ 1.937, 1.943) in **12a,b**. Also, the methyl signals in the *E* isomers (at δ 2.203 in **11a**, δ 2.206 in **11b**) appear downfield of the signals in the *Z* isomers (at δ 1.937 in **12a**, δ 1.943 in **12b**). This provides a convenient means of distinguishing between the geometric isomers. Full data are given in the Experimental Section.

(5) For purposes of clarity, transition states involving the same enantioface of the enone are depicted in each case; each TS has its enantiomeric counterpart involving reaction of the enantiomeric sulfoxide at the opposite enantioface of the enone.

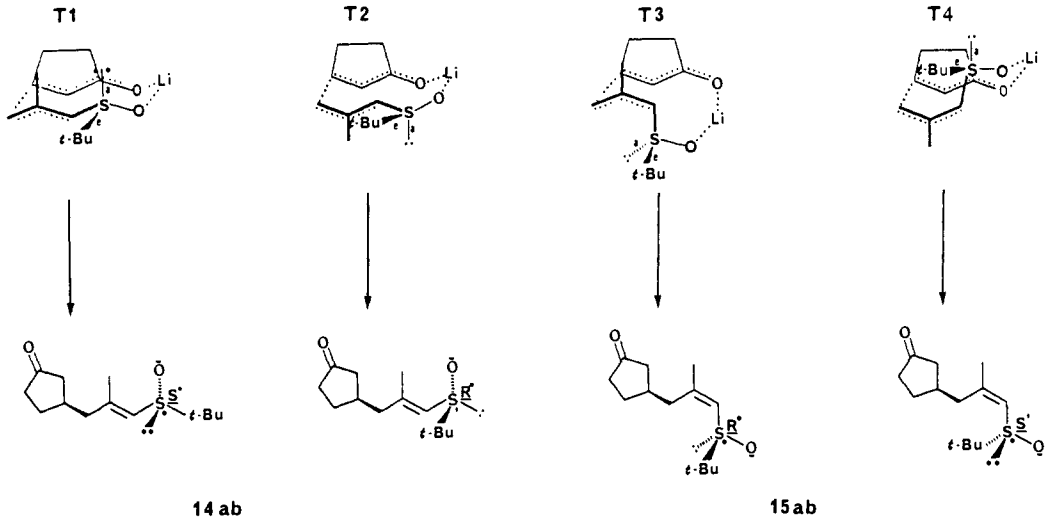


Figure 1. Transition-state representations for the reaction of transoid and cisoid lithiated sulfoxide **2** with cyclopentenone: T1, trans-fused chair–chair-; T2, cis-fused boat–boat-; T3, cis-fused chair–chair-; T4, cis-fused boat–chair-like transition states.

Table II. Chemical Shifts (δ) in Diastereomers of Products **16–18**[a]

proton	**16a**	**16b**	**17a**	**17b**	**18a**	**18b**
1′-Me	1.176	1.128	1.077	1.119	1.183	1.174
2′-Me	1.937	1.959	1.899	1.863	1.904	1.938
H3′	5.858	5.899	5.934	5.869	5.857	5.896
t-Bu	1.232	1.243	*b*	*b*	1.23	*b*

[a] Chemical shift of major diastereomer **a** (see Table I) given first. [b] Signal not able to be resolved.

endo orientation, as in T1 and T3, or an exo orientation, as in T2 and T4, relative to the enone. It is to be noted that the cisoid carbanion can only react through T3 and T4, which are clearly disfavored[6] with respect to T1 and T2.

The intercession of such transition states is also indicated by the reactions of the lithiated tiglyl and angelyl sulfoxides **3** and **4**. The first sulfoxide with cyclopentenone provides the (*E*)- and (*Z*)-vinylic sulfoxides **16a,b** and **17a,b**. As in the case involving the 2-methallyl sulfoxide **2**, the amount of (*Z*)-vinylic sulfoxides formed increases with temperature. Although the mixtures of diastereomers could not be separated, the relative proportions of each obtained as set out in Table I were easily determined through use of 400-MHz ^{1}H NMR spectroscopy. In Table II are set out the chemical shifts of selected protons of each diastereomer that were used as markers for determining the diastereomer ratios.[7] We describe below how the relative configurations of the major diastereomers are deduced.

Now, if the TS manifold has been reasonably represented in Figure 1, it is clear that the conjugate addition of the lithiated angelyl sulfoxide **4** to cyclopentenone will deliver diastereomers whose relative configurations must differ from those obtained from the tiglyl sulfoxide (as set out in Figure 3 below). This is indeed found to be the case, although at −70 °C only two products, **18a** and **18b**, are now obtained from sulfoxide **4** (Table I). The relative configuration of product **18a** is secured by an X-ray crystal structure study, the ORTEP plot from which is given in Figure 2.[8] The relative configuration at the allylic center is anti, and the relative configuration at sulfur is as for those vinylic sulfoxides obtained from 3-alkylallylic sulfoxides.[1] The double bond has *E*

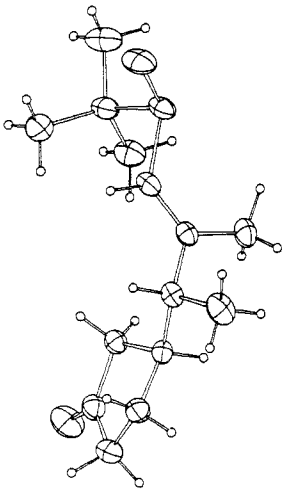


Figure 2. ORTEP plot of (1′*RS*,2′*E*,3*SR*,$R_S S_S$)-3-[3′-[(1,1-dimethylethyl)sulfinyl]-1′,2′-dimethylprop-2′-enyl]cyclopentanone (**18a**).

Table III. Chemical shifts (δ) in Sulfone Diastereomers from Products **16–18**

	sulfones from					
proton	**16a**	**16b**	**17a**	**17b**	**18a**	**18b**
1′-Me	1.201	1.159	1.106	1.157	1.201	1.159
2′-Me	2.125	2.167	1.943	1.902	2.125	2.161
H3′	6.012	6.050	5.995	~6.05	6.015	6.050
t-Bu	1.364	1.384	1.386	1.374	1.361	1.381

[a] Chemical shift of sulfone obtained from major diastereomer (see Table I) given first.

geometry; through correlation of ^{1}H NMR data of **18a** and **18b**, the latter is also shown to have this geometry.[9] Both products display chemical shifts in their ^{1}H NMR spectra that cannot be correlated with those of any diastereomer obtained from the tiglyl sulfoxide (Table II). However, by removal of the stereogenic center at sulfur a correlation can be made. The product mixtures from each of the angelyl and tiglyl sulfoxides were oxidized with *m*-chloroperbenzoic acid to the corresponding sulfone mixtures, which were assayed by NMR spectroscopy (Table III). It is noteworthy that the oxidation does not result in a decrease in the number of diastereomers within each set of products. Within

(6) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 204–208.

(7) The (*E*)- and (*Z*)-vinylic sulfoxides **16a,b** and **17a,b** are differentiated on the basis of chemical shifts of protons of the methyl group at C2′; as pointed out for compounds **11a,b** and **12a,b**,[4] those compounds in which the methyl signals appear at low field are the *E* compounds. It is also noted that coupling between H1′ and the protons of the methyl group at C1′ is consistently smaller in the *E* compounds **16a,b** ($J_{1',Me}$ = 6.3 Hz) than it is in the *Z* compounds **17a,b** ($J_{1',Me}$ = 7.2 Hz). These features are also characteristic of the corresponding sulfones (see Table III and the Experimental Section).

(8) Angles, bond lengths, least-squares coordinates, and thermal parameters are given in the supplementary material.

(9) Both compounds have $J_{1',Me}$ = 6.4 Hz. The chemical shift of the signal for the methyl group at C2′ in compound **18b** (δ 1.938) is characteristic of those of the *E* compounds **16a,b** from the tiglyl sulfoxide (Table II). These features are also consistently displayed in the spectra of the sulfones (see Table III and the Experimental Section).

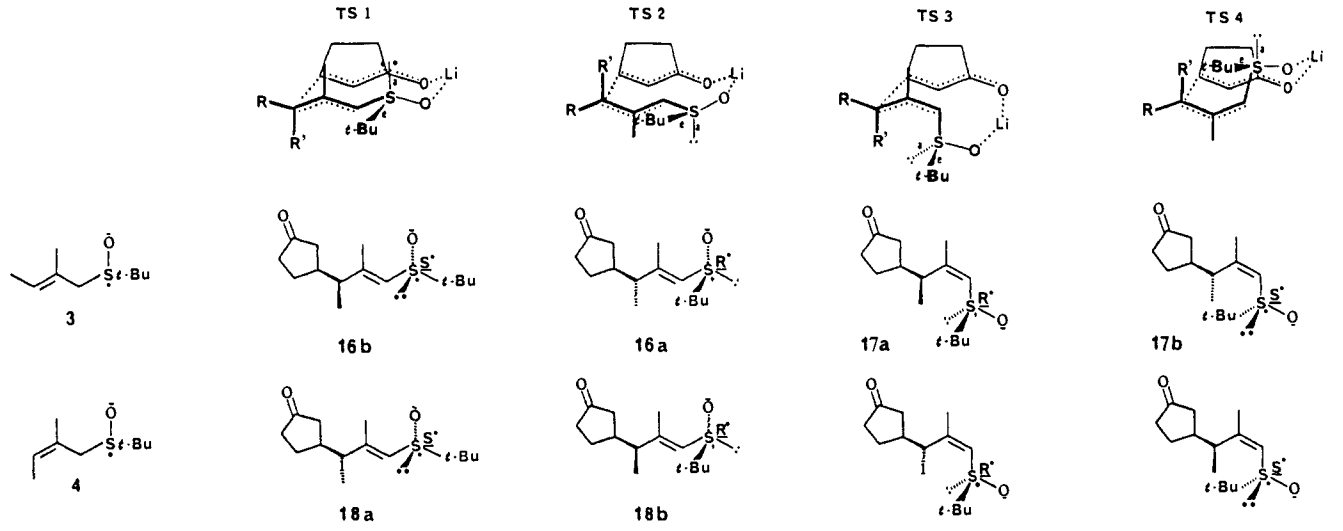


Figure 3. Products arising from reactions of lithiated transoid and cisoid tiglyl and angelyl sulfoxides **3** and **4** with cyclopentenone through trans-fused chair-chair-like TS (T1), cis-fused boat-boat-like TS (T2), cis-fused chair-chair-like TS (T3), and cis-fused boat-chair-like TS (T4). For each TS from tiglyl sulfoxide **3**, R = Me, R′ = H; for each TS from angelyl sulfoxide **4**, R = H, R′ = Me.

acceptable limits of measurement, it is seen that the major sulfone from the tiglyl system corresponds to the major sulfone from the angelyl system. Therefore, the sulfoxides from which these sulfones are derived differ in relative configuration solely at sulfur; the major product from the tiglyl sulfoxide is thus **16a**. The minor (*E*)-vinyl sulfone derived from the minor sulfoxide **16b** of the tiglyl system corresponds to the minor sulfone from the angelyl product **18b** (Table III). Thus, the sulfoxides **16b** and **18b** differ in relative configuration only at the sulfur atom; both must possess a relative configuration at the allylic center that is different from that in **18a**. Although it is not possible to assign relative configurations at sulfur in each of **16b** and **18b**, the known stereochemical features of these, and all the stereochemical features of the major *E* products **16a** and **18a**, can be entirely accommodated within the extended TS manifold described above. In Figure 3 are set out the four TS representations, and below these are given the structures of the products arising through each TS.[5] It becomes evident that the relative configuration at sulfur in **16b** must be S_S* as depicted, whereas in **18b** this must be R_S* as depicted. Furthermore, it is apparent why the tiglyl sulfoxide gives as major product **16a**, which with its anti configuration is atypical of normal products obtained from (*E*)-sulfoxides.[1] In T1, (1) eclipsing interactions involving the methyl group at C3 of the tiglyl system and the C3–C4 bond of the cyclopentenone and (2) diaxial interactions between the methyl group at C2 and the cyclopentenone disfavor T1 with respect to T2, where such interactions are absent. Nevertheless, a substantial amount of product **16b** is still obtained through T1, which in the absence of the foregoing interactions is normally of lower energy than T2.[6] For the angelyl sulfoxide, there is now an eclipsing interaction in T2 but not in T1, and the major product **18a** now obtained has the anti configuration characteristic of the reactions of (*Z*)-sulfoxides.[1] A small amount of product **18b** arises through T2 as a consequence of diaxial interactions in T1. Although we have not characterized the minor *Z* products **17a,b** arising from the tiglyl sulfoxide, we shall see below that the dominant *Z* product **17a** is most likely to possess the relative configuration corresponding to a reaction through T3, as given in Figure 3. It is significant that the angelyl sulfoxide does not give *Z* products. This can be explained on the basis of severe allylic strain experienced at the ground-state level, which destabilizes the cisoid lithiated angelyl sulfoxide, or 1,3-diaxial interactions within the angelyl system in T3 and T4. Be that as it may, the highly diastereoselective outcome of its conjugate addition stands in fascinating contrast to that of the tiglyl system; it is clear that any 2,3-disubstituted allylic sulfoxide, providing these substituents are trans, should undergo conjugate addition with high stereoselectivity.

In the case of the tiglyl and angelyl phosphine oxides **5** and **6**, the lithiated tiglyl phosphine oxide **5** reacts with cyclopentenone

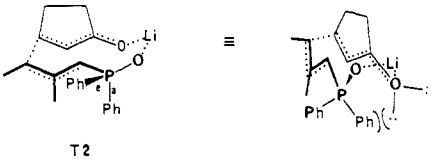
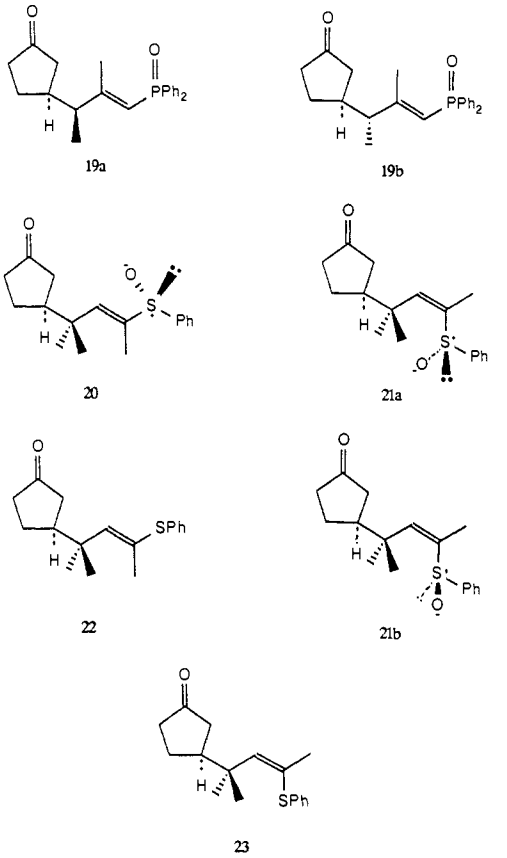


Figure 4. Cis-fused boat-boat-like TS (T2) of reaction between lithiated tiglyl phosphine oxide **5** and cyclopentenone illustrating interaction between diphenylphosphinoyl group and carbonyl oxygen.

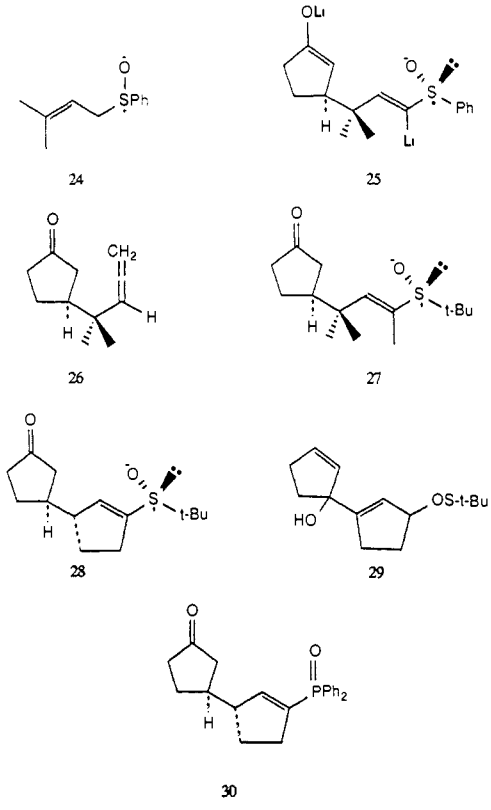
at −70 °C to give the vinylic phosphine oxides **19a** and **19b** in a ratio of 93:7 (79% overall). These *same* products are obtained



from the angelyl phosphine oxide **6**, with the latter now predominating (**19b**/**19a** 95:5, 76%). Both products are shown through ^{1}H NMR NOE difference experiments, in which the signal due to H3′ or to the methyl group at C2′ is unaffected upon preir-

radiation of the complementary site, to possess *E* double bonds. The relative configuration at the allylic centers in each product has not been unequivocally established, but it is reasonably assumed that the major product **19b** from the angelyl phosphine oxide has the same (anti) configuration as the major product **18a** derived from the angelyl sulfoxide. In view of this and the earlier work,[1] it is clear that the configuration in the tiglyl product **19a** must be syn.[10] As the major product **19a** from the tiglyl phosphine oxide **5** differs in relative configuration at C1′ from the major product **16a** from the tiglyl sulfoxide **3**, it seems that in T2 where a phenyl group of a phosphine oxide replaces the lone pair of a sulfoxide, then a stereoelectronic interaction is set up between the phenyl group and the pseudoaxial lone pair on the oxygen atom (Figure 4). This interaction is absent in T1, which does however experience a diaxial interaction between the pseudoaxial phenyl group attached to phosphorus and the C1–C5 bond of the cyclopentenone. The reaction of the tiglyl phosphine oxide with cyclopentenone provides an interesting contrast to the reaction of the tiglyl sulfoxide; the comparison thereby suggests another means of controlling the diastereoselectivity in these reactions through the attachment of large groups to the heteroatom.

1,3-Dialkylallyl Sulfoxides and Phosphine Oxides. The trimethylallyl phenyl sulfoxide (**7**), regardless of its mode of preparation (see Experimental Section), is obtained as a 1:1 mixture of diastereomers **7a,b** that cannot be separated.[11] The reaction of the lithiated mixture with cyclopentenone at −70 °C gives the vinylic sulfoxides **20** and **21a** in a 1:1 ratio (83% overall), whose geometries were determined by ^{1}H NMR NOE difference experiments.[12] That these products do differ in double-bond geometries and not just in configuration at sulfur was demonstrated by their reduction with tributylphosphine–iodine[13] to the sulfides **22** and **23**. In order to correlate the relative configuration at sulfur in sulfoxide **20** with that in the vinylic sulfoxides derived from 3-alkylallyl sulfoxides,[1] the 3,3-dimethylallyl sulfoxide **24**[1] was lithiated with lithium diisopropylamide (LDA) in the usual manner and treated with cyclopent-2-enone. The enolate produced in the conjugate addition was converted by butyllithium into the dianion **25**, whose treatment with methyl iodide at −70 °C yielded two products in a ratio of 93:7 (83% overall), the major of which is identical with that (**20**) obtained in the conjugate addition. The minor product according to the usual NMR criteria turns out to be the (*Z*)-vinylic sulfoxide **21b**, which is clearly different from that (**21a**) obtained in the conjugate addition.[12b] It may arise by isomerization either of the (*E*)-vinylic anion **25** to the *Z* anion prior to methylation—the isomerization of such carbanions has been reported previously[14,15]—or of the enolate precursor of the *E* product **20** produced in the methylation. In the latter case, this



24 25 26 27 28 29 30

can conceivably be brought about by addition–elimination involving the LDA and the vinyl sulfoxide in the enolate precursor of **20**. Treatment of either the sulfoxide **20** or, more conveniently, the mixture of sulfoxides **20** and **21a** obtained in the conjugate addition with excess of LDA at −70 °C indeed does result in formation of small and variable amounts (5–10%) of the sulfoxide **21b**, although the allene **26** is formed as the major product.[15] The mode of formation of sulfoxide **21b** indicates that it has the same relative configuration at the sulfur atom as the compound—either **20** or **25**—from which it is derived. Thus, the (*Z*)-sulfoxide **21a** formed in the conjugate addition has the *opposite* relative configuration at sulfur to that in both this sulfoxide and the (*E*)-sulfoxide **20** formed in the conjugate addition.

Although the relative amounts of the products **20** and **21a** formed in the conjugate addition correspond to the diastereomer ratio of the starting sulfoxides **7a,b**, the outcome of the reactions of the sulfoxides **8a,b** and **9a,b** suggests that this does not have any significance. The *tert*-butyl trimethylallyl sulfoxides are obtained from the corresponding sulfide also as an inseparable mixture of diastereomers **8a,b** in a ratio of 69:31. Unfortunately their lithiation and subsequent addition to cyclopentenone at −70 °C does not proceed cleanly and, although the (*E*)-vinylic sulfoxide **27** is produced, a number of other, possibly carbonyl addition, products that cannot be isolated are also formed. However, at −15 °C, the reaction proceeds so as to deliver the (*E*)-vinylic sulfoxide **27** (83%) and trace amounts of other uncharacterized products. That is, *each* diastereomer within the mixture is lithiated and largely reacts so as to give the *same* product. In contrast to previous cases, the diastereomeric mixture of the cyclopentenyl sulfoxides obtained in a ratio of 1:1 by oxidation of the corresponding sulfide, can be separated by flash chromatography into its less polar (**9a**) and more polar (**9b**) components. The individual diastereomers are quite stable and show no tendency to equilibrate at 0 °C during several weeks at least. Each upon lithiation and treatment with cyclopentenone at −70 °C gives the *single* vinylic sulfoxide **28** (30–40%) and a nonpolar highly unstable compound (30–40%) tentatively identified as the sulfenate ester **29**. The structure of the vinylic sulfoxide **28** was secured by an X-ray crystallographic study, the ORTEP plot of which is given in Figure 5.[8] The plot clearly indicates the anti configuration of the product such as is characteristic of vinylic sulfoxides obtained from

(10) A vinylic phosphine oxide obtained from an (*E*)-phosphine oxide related to the tiglyl phosphine oxide **5** is shown by X-ray crystallography to have a syn configuration: Haynes, R. K.; Vonwiller, S. C., unpublished results.

(11) It is evident that this represents an equilibrium ratio; although the diastereomers were able to be resolved by HPLC, immediate analysis of fractions separated by HPLC indicates complete reequilibration. The sulfoxide–sulfenate rearrangement that brings about the equilibration is especially favored in this case by the presence of the substituent at C1 and the aromatic group attached to sulfur: Bickart, P.; Carson, W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 2100.

(12) (a) Preirradiation at δ 6.419 (H2′) or 1.746 (H4′) did not induce enhancements at δ 1.746 or 6.419 in **20**, preirradiation at δ 1.702 (H4′) induced enhancements (6%) at δ 6.026 (H2′), and preirradiation at δ 6.026 induced enhancement (7%) at δ 1.702 in **21a**. In addition, signals (at δ 1.185 and 1.195) due to the methyl groups at C1′ in the *E* compound **20** appear upfield of those (at δ 1.375 and 1.446) in the *Z* compound **21a**. (b) In compound **21b** preirradiation at δ 6.146 (H2′) induced enhancement (9%) at δ 1.691 (H4′) and preirradiation at δ 1.691 induced enhancement (3%) at δ 6.146. Signals due to the methyl groups at C1′ appear at δ 1.373 and 1.452 (cf. compounds **21a** and **20**).

(13) Haynes, R. K.; Holden, M. *Aust. J. Chem.* **1982**, *35*, 517.

(14) Okamura, H.; Mitsuhira, Y.; Miura, M.; Takei, H. *Chem. Lett.* **1978**, 517.

(15) Posner, G. H.; Tang, P.-W.; Mallamo, J. P. *Tetrahedron Lett.* **1978**, 3995.

(16) This rearrangement will of course prevent the initial carbonyl adduct from undergoing dissociation–recombination to generate the conjugate adduct. The sulfenate ester is unaffected by treatment with LDA at −70 °C during 1 h.

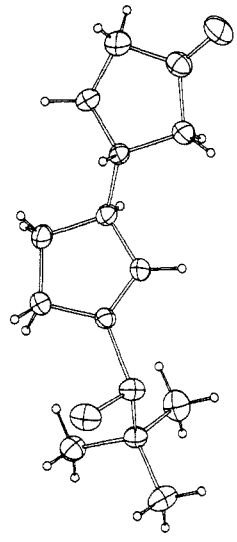


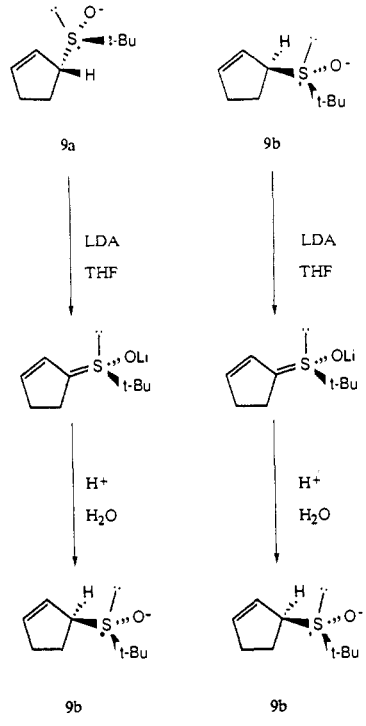
Figure 5. ORTEP plot of (1′*RS*,3*RS*,*S*$_s$,*R*$_s$)-3-[3′-[(1,1-dimethylethyl)-sulfinyl]cyclopent-2′-enyl]cyclopentanone (**28**). For crystallographic reasons, the plot is of the enantiomer of the structure depicted in the text.

(*Z*)-allylic sulfoxides.[1] The relative configuration at sulfur also conforms to that which is required of the trans-fused chair–chair-like transition state.[1] The sulfenate ester presumably arises by carbonyl addition of the lithiated sulfoxide to deliver the allylic sulfoxide, which then rearranges.[15] Finally, we find that the conjugate addition of the lithiated phosphine oxide **10** to cyclopentenone at −70 °C proceeds smoothly to give the vinylic phosphine oxide **30** (79%). Although the relative configuration of the product has not been established, this is assumed to be the same as that of the vinylic sulfoxide **28**.

Two important points emerge from these results. First, with respect to the reactions of the sulfoxides **7a,b**, the extended TS model predicts that the relative configuration at sulfur in the *Z* product **21a** will differ from that in the *E* product **20** when the former arises through T3 (Figure 6; cf. Figures 1 and 3). T3, on the basis of nonbonding interactions, is of lower energy than T4, but in the case of the reactions involving the sulfoxides **7a,b**, diaxial interactions involving the alkyl groups attached to the allyl system and the cyclopentenone ring further destabilize T4 with respect to T3, where such interactions are absent. Similarly, T1, normally of lower energy than T2, is now rendered much the more accessible of the transition states leading to *E* products through further destabilization of T2 (Figure 6). The lack of formation of *Z* products from the *tert*-butyl sulfoxides **8a,b** is surprising, although it may be noted that at −70 °C, the use of such a nonallylic substituent serves to suppress the formation of such products in the 2-methallyl system (Table I). The only TS seemingly accessible to the cyclopentenyl sulfoxides **9a** and **9b** and the phosphine oxide **10** is of course T1, and that the reaction does indeed proceed through T1 is confirmed by the relative configuration of the single vinylic sulfoxide **28** obtained from the sulfoxides.

The second important point relates to the formation of single vinylic sulfoxides from the diastereomeric allylic sulfoxides **7–9**. The conventional representation of a lithiated sulfoxide with lithium bound to both the α-carbon and oxygen[17,18] is not compatible with this observation. Rather, the result strengthens our assertion that the allylic carbanions at least are in fact planar at C1, with lithium bound to the oxygen atom. Deprotonation of a pair of diastereomeric sulfoxides will thus result in loss of

Scheme I



configurational identity at C1 as this site becomes planar in the lithiated sulfoxide. In support of this, we find that if the sulfoxides **8a,b** are lithiated and then quenched with aqueous ammonium chloride at −15 °C then the diastereomer ratio of the recovered sulfoxides **8a,b** is now 90:10.[19] The most dramatic and unequivocal confirmation of this loss of configurational identity is provided by lithiation–quenching of each of the cyclopentenyl sulfoxide diastereomers **9a** and **9b** at −70 °C. *The less polar diastereomer **9a** is thereby converted into the more polar diastereomer **9b**; the latter is returned intact after lithiation–quenching.*[20] The results of these simple experiments can be understood if it is assumed that lithiation of **9a** and of **9b** generates a single planar lithiated sulfoxide and that reprotonation is constrained to take place on the face away from the nonallylic group, as is illustrated in Scheme I. Kinetic protonation (deuteriation) of lithiated benzylic sulfoxides has been rationalized in terms of pyramidal carbanions, but it is emphasized that the stereochemical outcome of those reactions is equivalent to that described here.[18,21] The results further enable us to assign the relative configuration of the more polar diastereomer **9b** as (3*RS*,*R*$_S$*S*$_S$). It is clear that the conjugate addition reactions also proceed through the same face of the lithiated sulfoxide.

Conclusion

The concept of an extended transition state to account for the regiochemical and stereochemical outcome of the reactions of

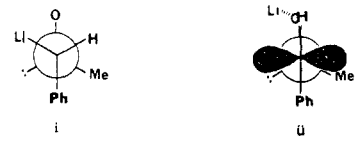
(17) Biellmann, J. F.; Vicens, J. J. *Tetrahedron Lett.* **1974**, 2915. Biellmann, J. F. Vicens, J. J. *Tetrahedron Lett.* **1978**, 467. Solladie, G. *Synthesis* **1981**, 185, and references cited therein. Wolfe, S.; LaJohn, L. A.; Weaver, D. F. *Tetrahedron Lett.* **1984**, *25*, 2863. Buses, M. A.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 4509. Williams, D. R.; Phillips, J. G.; White, F. H.; Huffman, J. C. *Tetrahedron* **1986**, *42*, 3003.

(18) Nakamura, K.; Higaki, M.; Adachi, S.; Oka, S.; Ohno, A. *J. Org. Chem.* **1987**, *52*, 1414, and references cited therein.

(19) We point out that the diastereomers **8a** and **8b** are in equilibrium, and this prevents accurate determination of the actual ratio of isomers produced upon quenching of the lithiated mixture.

(20) Lithiation–quenching was carried out by treating each diastereomer **9a** and **9b** with LDA in THF at −70 °C followed by quenching after 10 min with aqueous ammonium chloride. **9a** and **9b** are easily differentiated on the basis of their polarity and ^{1}H NMR spectra. The crude reaction mixtures obtained from each experiment contained no detectable quantities of **9a** (HPLC, NMR).

(21) Thus, lithiated benzyl methyl sulfoxide as represented in the Newman projection i in a recent report[18] becomes ii in a planar representation. Protonation (deuteriation) takes place on the *si* face.



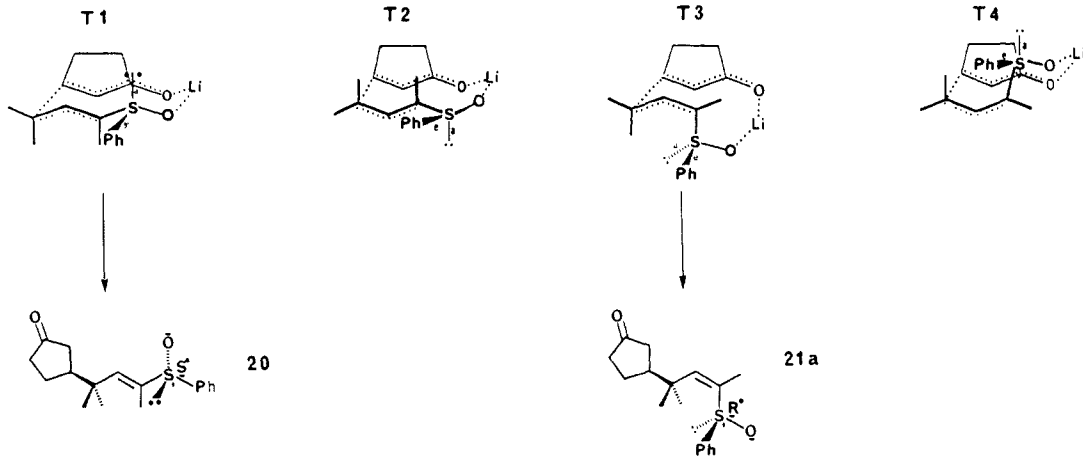


Figure 6. Products **20** and **21a** arising from reactions of lithiated transoid and cisoid sulfoxides **7a,b** through trans-fused chair–chair-like TS (T1) and cis-fused chair–chair-like TS (T3).

lithiated sulfoxides and phosphine oxides with cyclic enones as set out in the preceding paper is considerably strengthened by the results disclosed in the present paper. A crucial test of the generality of the model is to establish if it can account for the stereochemical outcome of reactions of allylic systems considerably more encumbered than those initially described and, indeed, it is remarkable how consistently and concisely the results obtained from these systems can be accommodated within the model. It is important to note that simple steric arguments are insufficient to account for the results. The number of diastereomers obtained from the tiglyl sulfoxide, for example, is the same as that obtained from the 2-methallyl system, even though there is present an extra stereogenic center in the products from the former sulfoxide. We have been able to delineate those systems that should react in diastereoselective fashion and have shown how diastereoselectivity can be improved through use either of sulfoxides bearing a large nonallylic substituent or of allylic systems bearing a stabilizing group larger than an alkyl or aryl sulfoxide.

The apparently low barrier to rotation about the C1–C2 bond in the lithiated 2-methallyl sulfoxides and the stereochemical convergence apparent in the reactions involving the diastereomeric allylic sulfoxides are both strongly indicative of a planar lithiated species in which the lithium counterion is presumably associated with the oxygen atom. It thereby has double-bond character between C1 and the sulfur atom and between C2 and C3. In other words, the lithiated species possesses a structure analogous to those of lithiated ketone or ester dienolates. This suggests that a range of structurally related reagents may display similar behavior toward cyclic enones as do the lithiated sulfoxides, phosphine oxides, and phosphonates, providing that these bear stabilizing substituents that suppress the tendency for reaction to proceed through C1. Thus, thio- and dithioester dienolates, nitronates derived from allylic nitro compounds, and ketone dienolates have the *potential* of reacting in this fashion. Finally, it must be emphasized that the enone is constrained according to the model to react through an s-trans conformation. Accordingly, for a successful outcome of reactions involving acyclic enones, these enones must be so substituted as to ensure that the s-trans conformers are predominantly populated under the conditions of the reactions. Our work in this area will be reported separately.

Experimental Section

Preparation of Allylic Sulfoxides and Phosphine Oxides. The general method of preparation is described in the accompanying paper.[1]

2-Methyl-1-(phenylsulfinyl)prop-2-ene (1). This was obtained from 2-methyl-1-(phenylthio)prop-2-ene[22] as a colorless liquid after flash chromatography with 40:60 ethyl acetate–light petroleum:[23] ^{1}H NMR (100 MHz) δ 1.90 (3 H, br s, $w_{h/2}$ = 2.5 Hz, CH_3), 3.35 (1 H, dd, J = 12.5, 0.8 Hz, H1α), 3.61 (1 H, dd, J = 12.5, 0.8 Hz, H1), 4.93 (1 H, br s, $w_{h/2}$ = 3.2 Hz, H3), 5.18 (1 H, dq, J = 1.5, 1.4 Hz, H3), 7.4–7.8 (5 H, m, C_6H_5).

3-[(1,1-Dimethylethyl)sulfinyl]-2-methylprop-1-ene (2). Treatment of 3-chloro-2-methylprop-1-ene (2.22 g, 24.5 mmol) with sodium 2-methylpropane-2-thiolate (23 mmol) in methanol (30 mL) gave the sulfide (2.9 g, 86%) as a colorless liquid: bp 76 °C (26 mm; Kugelrohr); IR (neat) ν_{max} 2980–2850 (s), 1640 (w), 1460 (s), 1365 (s), 1280 (w), 1210 (sh, m), 1165 (s), 1060–1010 (br, m), 895 (s) cm^{-1}; ^{1}H NMR (100 MHz) δ 1.33 (9 H, s, *t*-Bu), 1.84 (3 H, dd, J = 1.3, 0.9 Hz, CH_3), 3.19 (2 H, d, J = 0.9 Hz, H1), 4.82 (1 H, m, J = 1.4 Hz, H3), 4.93 (1 H, ddq, J = 0.9, 0.9, 0.9 Hz, H3); MS (CI) *m/e* 144 (M, 79), 89 (21), 88 (77), 59 (23), 58 (21), 57 (100), 56 (60), 55 (85), 54 (33), 41 (86), 39 (44), 29 (71). The compound was characterized by conversion into the sulfoxide **2** obtained as a colorless liquid: bp 110 °C (0.8 mm; Kugelrohr); IR (neat) ν_{max} 2950 (s), 1639 (w), 1459 (m), 1364 (m), 1281 (w), 1157 (w), 1048 (s), 1011 (sh, m), 893 (m), cm^{-1}; ^{1}H NMR δ 1.280 (9 H, s, *t*-Bu), 1.920 (3 H, dd, J = 1.4, 1.0 Hz, CH_3), 3.078 (1 H, dd, J = 12.3, 0.75 Hz, H1), 3.190 (1 H, dd, J = 12.3, 1.05 Hz, H1), 5.058 (1 H, ddq, J = 1.05, 0.75, 1.4 Hz, H3), 5.082 (1 H, dq, J = 1.4, 1.4 Hz, H3); MS *m/e* 160 (M, 3), 104 (5), 57 (100), 55 (32), 41 (35), 29 (32), 28 (26); HRMS calcd for $C_8H_{16}SO$ 160.0921, found, 160.0934.

(*E*)-1-[(1,1-Dimethylethyl)sulfinyl]-2-methylbut-2-ene (3). Phosphorus tribromide (3.14 g, 11.6 mmol, 1.10 mL) was added dropwise to (*E*)-2-methylbut-2-en-1-ol[24] (2.0 g, 23.2 mmol) in dry diethyl ether (50 mL) at −10 °C. The solution was stirred for a further 2 h, washed with aqueous potassium carbonate and brine solutions, and dried (Na_2SO_4). The solvent was removed by distillation at atmospheric pressure to leave the allylic bromide (2.33 g, 67%) as a pale yellow lachrymatory liquid, which was used without further purification: ^{1}H NMR (90 MHz) δ 1.60 (3 H, d, $J \simeq$ 6.9 Hz, H4), 1.78 (3 H, br s, CH_3), 3.99 (2 H, s, H1), 5.66 (1 H, q, $J \simeq$ 6.9 Hz, H3). Treatment of the bromide (2.31 g, 15.5 mmol) with sodium 2-methylpropane-2-thiolate (15.5 mmol) in methanol (25 mL) at 0 °C under nitrogen gave the sulfide (2.12 g, 86%) as a colorless liquid: bp 138 °C (34 mm; Kugelrohr); IR (neat) ν_{max} 2950 (s), 2915 (m), 2910 (m), 1465 (s), 1450 (m), 1385 (m), 1365 (s), 1170 (s), 1038 (m) cm^{-1}; ^{1}H NMR (90 MHz) δ 1.33 (9 H, s, *t*-Bu), 1.57 (3 H, dq, J = 6.9, 1.0 Hz, H4), 1.70 (3 H, dq, $J \simeq$ 1.5, 1.0 Hz, CH_3), 3.16 (2 H, br s, $w_{h/2}$ = 3 Hz, H1), 5.41 (1 H, dq, J = 6.8, 1.2 Hz, H3); MS (CI) *m/e* 159 (M + 1, 20), 158 (M, 77), 102 (66), 101 (51), 69 (89), 68 (89), 67 (21), 59 (31), 57 (100), 55 (21), 41 (90), 39 (34), 29 (100). Anal. Calcd for $C_9H_{18}S$: C, 68.3; H, 11.5. Found: C, 68.6; H, 11.5. The sulfide was oxidized to the sulfoxide; after purification by flash chromatography with diethyl ether, this was obtained as a colorless oil, which froze as large needles at 5 °C: IR (neat) ν_{max} (thin film) 2955 (s), 2910 (s), 2855 (m), 1460 (m), 1440 (w), 1380 (w), 1361 (m), 1292 (m), 1115 (m), 1039 (s), 1010 (sh, m), 940 (w), 920 (w), 870 (w), 829 (w), 728 (m) cm^{-1}; ^{1}H NMR δ 1.151 (9 H, s, *t*-Bu, 1.57 (3 H, ddq, J = 6.8, 1.0, 0.9 Hz, H4), 1.683 (3 H, dq, J = 1.3, 1.3 Hz, CH_3), 2.91 (1 H, ddq, J = 12.6, 0.8, 0.8 Hz, H1), 3.12 (1 H, ddq, J = 12.6, 1.2, 1.2 Hz, H1), 5.46 (1 H, ddqq, J = 6.8, 1.4, 1.3, 0.9 Hz, H3); MS *m/e* 349 (2M + 1, 44), 175 (M + 1, 80), 123 (38), 119 (50), 118 (24), 101 (62), 70 (38), 69 (100), 57 (99), 55 (29), 41 (92), 39 (46), 29 (99), 28 (26). Anal. Calcd for $C_9H_{18}OS$; C, 62.0; H, 10.4. Found: C, 61.7; H, 10.4.

(*Z*)-1-[(1,1-Dimethylethyl)sulfinyl]-2-methylbut-2-ene (4). (*Z*)-2-Methylbut-2-en-1-ol[25] (2.202 g, 25.6 mmol) was treated with phosphorus

(22) Parham, W. E.; Green, S. H. *J. Org. Chem.* **1965**, *30*, 728.
(23) Antonjuk, D. J.; Ridley, D. D.; Smal, M. A. *Aust. J. Chem.* **1980**, *33*, 2635.
(24) Hatch, L. F.; Noyes, P. R. *J. Am. Chem. Soc.* **1957**, *79*, 345.
(25) Zaidlewicz, M.; Uzarewicz, A.; Sarnowski, R. *Synthesis* **1979**, 62.

tribromide (3.465 g, 12.8 mol, 1.22 mL) to give the allylic bromide (2.52 g, 58%) as a colorless liquid, which was used without further purification: ^{1}H NMR δ 1.65 (3 H, br d, $J_{4,3} \simeq 6.6$ Hz, H4), 1.82 (3 H, br s, CH_3), 3.96 (2 H, s, H1), 5.44 (1 H, q, $J_{3,4} \simeq 6.6$ Hz, H3). The bromide (860 mg, 5.79 mmol) was treated with sodium 2-methylpropane-2-thiolate (5.79 mmol) in methanol according to the usual conditions to give the sulfide (750 mg, 82%) as a colorless liquid: ^{1}H NMR (90 MHz) δ 1.35 (9 H, s, *t*-Bu), 1.62 (3 H, br d, $J_{4,3} = 6.9$ Hz, H4), 1.80 (3 H, br s, $w_{h/2} = 4.5$ Hz, CH_3), 3.18 (2 H, s, H1), 5.28 (1 H, br q, $J_{3,4} = 6.9$ Hz, H3). This was oxidized directly without further purification to give the sulfoxide (729 mg, 89%) as a colorless oil: NMR analysis indicated that it was isomerically pure and was uncontaminated by sulfone; IR (neat) ν_{max} 2968 (s), 2928 (s), 2868 (m), 1474 (w), 1460 (m), 1367 (m), 1182 (w), 1072 (m), 1049 (s), 1031 (s), 821 (m) cm^{-1}; ^{1}H NMR (100 MHz) δ 1.30 (9 H, s, *t*-Bu), 1.68 (3 H, dddq, J = 6.6, 1.4, 0.8, 0.7 Hz, H4), 1.88 (3 H, dq, J = 1.5, 1.5 Hz, CH_3), 3.19 (1 H, ddq, J = 12.6, 0.8, 0.9 Hz, H1α), 3.27 (1 H, ddq, J = 21.5, 0.5, 0.5 Hz, H1β), 5.63 (1 H, ddqq, J = 6.9, 1.6, 1.0, 0.5 Hz, H3); MS (CI) *m/e* 175 (M + 1, 12), 119 (23), 101 (26), 69 (64), 57 (77), 41 (100), 39 (15), 30 (39). Anal. Calcd for $C_9H_{18}OS$: C, 62.0; H, 10.4. Found: C, 61.9; H, 10.6.

2-Methyl-4-(phenylsulfinyl)pent-2-ene (7a,b). Treatment of sodium benzenethiolate (50 mmol) in methanol (120 mL) with 4-bromo-2-methylpent-2-ene[26] (8 g, 50 mmol) according to the usual conditions gave the sulfide[27] (6.9 g, 72%) as a pale yellow liquid: bp 110–115 °C (0.1 mm; Kugelrohr); IR (neat) ν_{max} 2930 (br, s), 1440 (s), 1470 (s), 1210 (w), 1090 (w), 1030 (w), 850 (m), 760 s, 700 s, 700 s cm^{-1}; ^{1}H NMR (90 MHz) δ 1.28 (3 H, d, J = 6.6 Hz, H5), 1.40 (3 H, d, J = 1.3 Hz, CH_3), 1.61 (3 H, d, J = 1.3 Hz, H1), 3.96 (1 H, dq, J = 9.9, 6.6 Hz, H4), 5.06 (1 H, dqq, J = 9.9, 1.3, 1.3 Hz, H3), 7.15–7.45 (5 H, m, C_6H_5); MS *m/e* 192 (M$^+$, 1), 164 (2), 110 (5), 109 (s), 83 (40), 82 (65), 81 (15), 77 (5), 67 (100). The sulfide was also obtained in the following way. 4-Methylpent-3-en-2-ol (2.0 g, 20 mmol) and benzenethiol (2.2 g, 20 mmol) in dichloromethane (50 mL) containing trifluoroacetic acid (4.5 g, 40 mmol) at −70 °C was stirred for 2 h. The reaction mixture was then poured into ice water and extracted with diethyl ether. The extracts were washed with aqueous potassium carbonate and brine and then dried (Na_2SO_4). Evaporation of the solvent under reduced pressure and distillation of the residual oil under the above conditions gave the sulfide (3.1 g, 81%). Oxidation of the sulfide gave after flash chromatography with 40:60 ethyl acetate–light petroleum a 1:1 mixture of diastereomers **7a,b** of the sulfoxide as a colorless oil. As the isomers equilibrate under HPLC conditions, they could not be separated: IR (neat) ν_{max} 2960 (s), 1450 (s), 1100 (m), 1070 (s), 760 (s), 700 (m) cm^{-1}; ^{1}H NMR (isomer a) δ 1.26 (3 H, d, J = 6.8 Hz, H5), 1.44 (3 H, d, J = 1.31 Hz, CH_3), 1.71 (3 H, d, J = 1.35 Hz, H1), 3.67 (1 H, dq, J = 9.75, 6.8 Hz, H4), 4.76 (1 H, dqq, J = 9.75, 1.3, 1.3 Hz, H3), 7.45–7.65 (5 H, m, C_6H_5); ^{1}H NMR (isomer b) δ 1.15 (3 H, d, J = 1.37 Hz, H1), 1.36 (3 H, d, J = 6.8 Hz, H5), 1.68 (3 H, d, J = 1.31 Hz, CH_3), 3.52 (1 H, dq, J = 10.5, 6.8 Hz, H4), 4.94 (1 H, dqq, J = 10.5, 1.3, 1.3 Hz, H3), 7.45–7.65 (5 H, m, C_6H_5); MS *m/e* 208 (M$^+$, 2), 126 (62), 125 (20), 110 (30), 109 (40), 97 (13), 83 (100), 82 (30), 78 (70), 77 (50), 65 (77). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.2; H, 7.7; S, 15.4. Found: C, 69.4; H, 7.8; S, 15.0.

4-[(1,1-Dimethylethyl)sulfinyl]-2-methylpent-2-ene (8a,b). A solution of 4-methylpent-3-en-2-ol (5.0 g, 50 mmol) and 2-methylpropane-2-thiol (4.51 g, 50 mmol) in dichloromethane (50 mL) containing trifluoroacetic acid (11.4 g, 100 mmol) at −60 °C under nitrogen was stirred for 1 h. Workup as described above gave the sulfide (7.4 g, 86%) as a pale yellow liquid: bp 90–95 °C (20 mm) [lit.[28] bp 80 °C (10 mm)]; ^{1}H NMR (90 MHz) δ 1.23 (3 H, d, J = 6.9 Hz, H5), 1.31 (9 H, s, *t*-Bu), 1.66 (6 H, s, H1, CH_3), 3.67 (1 H, dq, J = 9.8, 6.9 Hz, H_2), 5.08 (1 H, d, J = 9.8 Hz, H3). Oxidation of the sulfide gave after flash chromatography with 30:70 ethyl acetate–light petroleum a 69:31 mixture of diastereomers **8a,b** of the sulfoxide. Although the diastereomers were able to be resolved by analytical HPLC, these underwent equilibration under preparative HPLC conditions and so could not be separated: IR (neat) ν_{max} 2950 (s), 1440 (s), 1360 (m), 1175 (w), 1040 (s) cm^{-1}; ^{1}H NMR δ (major isomer) 1.25 (9 H, s, *t*-Bu), 1.33 (3 H, d, J = 7.25 Hz, H5), 1.71 (3 H, d, J = 1.2 Hz, H1), 1.73 (3 H, d, J = 1.2 Hz, CH_3), 3.60 (1 H, dq, J = 10.4, 7.0 Hz, H4), 5.16 (1 H, dm, J = 10.4 Hz, H3); ^{1}H NMR (minor isomer) 1.24 (9 H, s, *t*-Bu), 1.40 (3 H, d, J = 7.25 Hz, H5), 1.68 (3 H, d, J = 1.2 Hz, H1), 1.77 (3 H, d, J = 1.2 Hz, CH_3), 3.51 (1 H, dq, J = 10.0, 7.25 Hz, H2), 5.41 (1 H, dm, J = 10.0 Hz, H3); MS (CI) *m/e* 189 (P + 1). Anal. Calcd for $C_{10}H_{20}OS$: C, 63.9; H, 10.6. Found: C, 63.8; H, 10.6.

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(27) Hartmann, J.; Muthukrishnan, R.; Schlosser, M. *Helv. Chim. Acta* **1974**, *57*, 2261.
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3-[(1,1-Dimethylethyl)sulfinyl]cyclopent-1-ene (9a,b). Treatment of sodium 2-methylpropane-2-thiolate (125 mmol) in methanol (125 mL) with 3-chlorocyclopent-1-ene (12.9 g, 125 mmol) gave the sulfide (12.3 g, 63%) as a colorless liquid: bp 90–95 °C (0.1 mm); IR (neat) ν_{max} 2860 (s), 1460 (m), 1360 (m), 1160 (s), 1020 (w), 740 (m) cm^{-1}; ^{1}H NMR δ 1.37, (9 H, s, *t*-Bu), 1.89–1.98 (1 H, m, H4β), 2.26–2.56 (3 H, m, H4α, H5), 3.84–3.92 (1 H, m, H3α), 5.71 (1 H, dddd, J = 5.75, 2.3, 1.8, 1.8 Hz, H2), 5.79 (1 H, dddd, J = 5.75, 2.3, 2.3, 1.8 Hz, H2); MS *m/e* 156 (M$^+$, 62), 100 (20), 99 (25), 98 (30), 97 (35), 90 (18), 89 (20), 85 (18), 83 (23), 67 (70), 57 (30); HRMS calcd for $C_9H_{16}S$ 156.0973, found 156.0972. Oxidation of the sulfide gave the sulfoxide as a mixture of two diastereoisomers in the ratio 1:1. The diastereomers were separated by flash chromatography with 35:65 ethyl acetate–light petroleum and further purified by HPLC with 70:30 ethyl acetate–light petroleum (Whatman Partisil 10 M20 column, flow rate 13 mL min^{-1}, 600 psi). The less polar isomer **9a**, $_T$ 59 min, assumed to be the ($3RS,S_sR_s$) isomer, was a colorless liquid, which solidified at 4 °C: IR (neat) ν_{max} 3060 (w), 2940 (s), 1460 (s), 1360 (s), 1280 (w), 1180 (m), 1020 (s), 910 (m), 740 (m) cm^{-1}; ^{1}H NMR δ 1.27 (9 H, s, *t*-Bu), 2.01 (1 H, dddd, J = 14.0, 9.2, 9.2, 5.8 Hz, H4β), 2.36–2.46 (1 H, m, H5β), 2.47–2.58 (1 H, m, H5α), 2.63 (1 H, dddd, J = 13.9, 9.0, 4.4, 4.4 Hz, H4α), 3.81–3.88 (1 H, m, H3α), 5.67 (1 H, dddd, J = 5.7, 2.3, 1.8, 1.8 Hz, H2), 6.08 (1 H, dddd, J = 5.7, 2.3, 2.3, 1.8 Hz, H1); MS *m/e* 172 (M$^+$, 1), 106 (10), 84 (8), 67 (100), 66 (29), 65 (12), 57 (50). Anal. Calcd for $C_9H_{16}OS$: C, 62.8; H, 9.3. Found: C, 62.6; H, 9.3.

The more polar isomer **6b**, R_f 85 min, assumed to be the ($3RS,R_sS_s$) isomer was a white solid: mp 45–47 °C; IR (neat) ν_{max} 2950 (s), 1460 (s), 1360 (s), 1280 (w), 1180 (m), 1020 (s), 910 (m), 740 (m) cm^{-1}; ^{1}H NMR δ 1.30 (9 H, s, *t*-Bu), 2.04 (1 H, dddd, J = 13.9, 9.2, 9.1, 5.6 Hz, H4β), 2.20 (1 H, dddd, J = 13.9, 9.0, 4.4, 4.4 Hz, H4α), 2.39–2.50 (1 H, m, H5β), 2.53–2.65 (1 H, m, H5α), 3.93–4.00 (1 H, m, H3α), 5.83 (1 H, dddd, J = 5.7, 2.3, 1.8, 1.8 Hz, H2), 6.18 (1 H, dddd, J = 5.7, 2.3, 2.3, 1.8 Hz, H1); MS *m/e* 172 (M$^+$, 1), 106 (6), 84 (4), 67 (100), 57 (34). Anal. Calcd for $C_9H_{16}OS$: C, 62.8; H, 9.3. Found: C, 62.7; H, 9.2.

(*E*)-(2-Methylbut-2-enyl)diphenylphosphine Oxide (5). Butyllithium (10.0 mL, 13.4 mol, 1.34 M in hexane) was added to a stirred solution of diphenylphosphine (2.50 g, 13.4 mmol, 2.33 mL) in THF (50 mL) at −40 °C under nitrogen. After 5 min, a solution of 1-bromo-2-methylbut-2-ene (2.0 g, 13 mmol) in THF (7 mL) was added dropwise to the orange-red anion at −25 °C. The reaction mixture was warmed to 0 °C, quenched with aqueous hydrogen peroxide (5%, 50 mL), and then extracted with diethyl ether and chloroform. The combined extracts were washed consecutively with aqueous sodium sulfite, aqueous potassium carbonate, and brine and then dried (Na_2SO_4). Evaporation of the solvents left a white solid (3.85 g), which was crystallized from ethyl acetate–light petroleum to give the phosphine oxide (2.76 g, 76%) as small prisms: mp 117–120 °C; IR ($CHCl_3$) ν_{max} 2982 (s), 1975 (w), 1907 (w), 1484 (w), 1439 (s), 1405 (w), 1384 (m), 1221 (sh), 1179 (s), 1146 (m), 1119 (s), 1105 (m), 849 (m) cm^{-1}; ^{1}H NMR (100 MHz) δ 1.51 (3 H, dd, J = 6, 6 Hz, H4), 1.67 (3 H, br s, $w_{h/2} = 6$ Hz, CH_3), 3.07 (2 H, br d, J = 13.8 Hz, H1), 5.19 (1 H, br dq, $J \simeq 6, 5$ Hz, H3), 7.35–7.90 (10 H, m, C_6H_5); MS *m/e* 271 (M + 1, 10), 270 (M, 51), 203 (12), 202 (100), 201 (73), 145 (12), 77 (27), 57 (12), 51 (12), 47 (17), 41 (13). Anal. Calcd for $C_{17}H_{19}OP$: C, 75.5; H, 7.1. Found: C, 75.8; H, 6.9.

(*Z*)-(2-Methylbut-2-enyl)diphenylphosphine Oxide (6). (*Z*)-(2-Methylbut-2-enyl)diphenylphosphine oxide was prepared by the same procedure as that described above from diphenylphosphine (1.09 g, 5.9 mmol, 1.02 mL) and (*Z*)-1-bromo-2-methylbut-2-ene (872 mg, 5.85 mmol). Recrystallization from ethyl acetate–light petroleum gave the phosphine oxide **6** as fine needles (1.13 g, 71%): mp 117–119 °C (lit.[29] mp 116 °C); ^{1}H NMR (100 MHz) δ 1.19–1.39 (3 H, m, H4), 1.76 (3 H, m, $J \simeq 1.5, 1.5, 1.5$ Hz, CH_3), 3.13 (2 H, br d, J = 14.3, H1), 5.38 (1 H, dq, $J \simeq 7, 6$ Hz, H3), 7.35–7.95 (10 H, m, C_6H_5).

Cyclopent-2-enyldiphenylphosphine oxide (10). This was obtained from diphenylphosphine (20.0 g, 107 mmol) and 3-chlorocyclopent-1-ene (11 g, 107 mmol) according to the above procedure as a pale yellow viscous oil. The product was purified by flash chromatography with 65:35 ethyl acetate–light petroleum to give the phosphine oxide (20.9 g, 73%), as prisms: mp 126–128 °C; IR ($CHCl_3$) ν_{max} 2950 (s), 1590 (w), 1490 (s), 1430 (s), 1170 (s), 1120 (s), 1000 (w), 910 (s) cm^{-1}; ^{1}H NMR δ 2.10–2.40 (4 H, m, H4, H5), 3.65–3.75 (1 H, m, H1), 5.53–5.60 (1 H, m, H2), 5.91–5.97 (1 H, m, H1), 7.42–7.84 (10 H, m, C_6H_5); MS *m/e* 268 (M$^+$, 18), 203 (28), 202 (100), 201 (73), 183 (10), 155 (20), 125 (18), 77 (50), 67 (15). Anal. Calcd for $C_{17}H_{17}OP$: C, 76.1; H, 6.3. Found: C, 76.1; H, 6.4.

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Conjugate Addition Reactions. 2-Methyl-1-(phenylsulfinyl)prop-2-ene (1). From the sulfoxide (216 mg, 1.20 mmol) and cyclopent-2-enone (126 mg, 1.53 mmol) according to the usual conditions[1] at −70 °C was obtained a yellow viscous oil (316 mg). This was chromatographed with 20:80 ethyl acetate–diethyl ether to give the conjugate adducts **11a,b** and the carbonyl adducts **13a,b** (218 mg, 69% overall) in a ratio of 82:18 and the sulfoxide **1** (37 mg, 17%). These were further purified by flash chromatography to give first *(E)-3-[2'-methyl-3'-(phenylsulfinyl)prop-2'-enyl]cyclopentanone* (**11a,b**) as a 1:1 mixture of diastereomers: IR (neat) ν_{max} 2950 (m), 1732 (s), 1622 (w), 1441 (m), 1401 (w), 748 (s), 689 (m) cm^{-1}; ^1H NMR δ 1.40–1.598 (1 H, m, H4β), 1.724, 1.795 (1 H, dd, J = 17.3, 9.0 Hz, H2β), 2.012–2.495 (7 H, m, H2α, H3, H4α, H5, H1'), 2.203, 2.206 (3 H, d, J = 1.0 Hz, CH_3), 6.065, 6.068 (1 H, q, J = 1.0 Hz, H3'), 7.41–7.64 (5 H, m, C_6H_5); preirradiation at δ 6.06 (H3') resulted in enhancement at δ 2.28 (H2') of 4.4%; MS m/e 262 (M, 11), 246 (28), 163 (55), 135 (24), 131 (72), 110 (56), 109 (26), 93 (23), 91 (29), 83 (60), 78 (26), 77 (35), 55 (100), 53 (27), 51 (24), 41 (59), 28 (100); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1035. Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.7; H, 6.9. Found: C, 68.4; H, 6.9.

Next, *(Z)-1-[2'-methyl-3'-(phenylsulfinyl)prop-2'-enyl]cyclopent-2-en-1-ol* (**13a,b**) was obtained as a 48:52 mixture of diastereomers: IR ν_{max} 3600–3150 (s), 3050 (m), 2930 (m), 1408 (w), 1380 (w), 1178 (m), 1087 (m), 1041 (s), 1021 (s), 1000 (m), 930 (m), 810 (m), 750 (m), 735 (m), 696 (w) cm^{-1}; ^1H NMR (* denotes minor diastereomer **13b**) δ 1.927–2.590 (4 H, m, H4, H5), 2.020, 2.034* (3 H, d, J = 1.2 Hz, CH_3) 2.946* (2 H, s, H1'), 2.936 (1 H, d, J = 13.4 Hz, H1'), 2.998 (1 H, d, J = 13.4 Hz, H1'), 5.736*, 5.827 (1 H, dt, J = 5.8, 2.2 Hz, H2) 5.952*, 5.968 (1 H, dt, J = 5.8, 2.4 Hz, H3), 6.166 (1 H, q, J = 1.2 Hz, H3') 7.43–7.71 (5 H, m, C_6H_5); preirradiation at δ 6.16 (H3') gave enhancement at δ 2.03 of 5.8%, preirradiation at δ 2.03 (CH_3) gave enhancements at δ 6.16 of 2.0%, at δ 5.74 of 0.3%, and at δ 5.83 of 0.3%; MS m/e 262 (M, <1), 246 (M − O, 3), 245 (M − OH, 3), 244 (M − H_2O, 3), 227 (15), 180 (30), 163 (55), 135 (40), 117 (100), 110 (39), 109 (22), 91 (40), 83 (55), 82 (38), 43 (22), 41 (37), 39 (60), 29 (24), 28 (56); HRMS calcd for [$C_{15}H_{18}O_2S$ − H_2O] 244.0924, found 244.0921.

Deprotonation of the sulfoxide **1** (303 mg, 1.68 mmol) at −70 °C followed by addition of cyclopent-2-enone (153 mg, 1.85 mmol) to the solution at −10 °C gave a 74:26 mixture of the conjugate adducts **11a,b** and **12a,b** as a pale yellow oil (407 mg, 93%). Separation of the mixture by HPLC with 70:30 ethyl acetate–light petroleum (Waters semipreparative μ-Porasil column, flow rate 3 mL/min, 350 psi) gave a 75:25 mixture of the diastereomers **12a,b** of *(Z)-3-[2'-methyl-3'-(phenylsulfinyl)prop-2'-enyl]cyclopentanone*. The mixture was resubmitted to HPLC with 80:20 ethyl acetate–light petroleum (80:20) (Whatman 10 M20 column, 13 mL min^{-1}, 800 psi). The first isomer eluted (R_t 78 min) was the minor diastereomer **12b**, obtained as a white solid: mp 113–116 °C; IR ($CHCl_3$) ν_{max} 2929 (s), 2855 (sh), 1739 (s), 1445 (m), 1158 (m), 1059 (s), 1021 (s), 998 (m) cm^{-1}; ^1H NMR δ 1.59–1.71 (1 H, m, H4β), 1.943 (3 H, d, J = 1.4 Hz, CH_3), 1.99–2.56 (6 H, m, H2, H3, H4, H5), 2.78 (2 H, d, J = 7.3 Hz, H1'), 6.1704 (1 H, q, J = 1.4 Hz, H3'), 7.46–7.63, m, C_6H_5); preirradiation at δ 6.1704 (H3') gave enhancement (5.6%) at δ 1.943 (CH_3), preirradiation at δ 1.943 gave enhancement (3%) at δ 6.1704; MS m/e 262 (M^+, 9), 246 (27), 245 (100), 180 (7), 163 (43), 137 (18), 135 (33), 131 (19), 110 (20), 109 (18), 93 (60); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.0986.

The major isomer **12a**, a colorless oil, was eluted next (R_t 82 min): IR ($CHCl_3$) ν_{max} 2929 (s), 2855 (sh), 1739 (s), 1445 (m), 1405 (w), 1158 (m), 1059 (s), 1021 (s), 998 (m) cm^{-1}; ^1H NMR δ 1.73–1.35 (1 H, m, H4β), 1.937 (3 H, d, J = 1.0 Hz, CH_3), 2.15–2.59 (6 H, m, H2, H3, H4, H5), 2.701 (1 H, dd, J = 13.7, 7.3 Hz, H1'), 2.835 (1 H, dd, J = 13.7, 7.3 Hz, H1'), 6.1698 (1 H, q, J = 1.0 Hz, H3'), 7.46–7.63 (5 H, m, C_6H_5); preirradiation at δ 6.1698 (H3') gave enhancement (3%) at δ 1.937 (CH_3), preirradiation at δ 1.937 gave enhancement (2.5%) at δ 6.1698; MS m/e 262 (M^+, 10), 246 (41), 245 (100), 163 (73), 137 (20), 135 (40), 131 (25), 110 (31), 109 (31), 93 (62); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1024.

The sulfoxide **1** (412 mg, 2.29 mmol) was deprotonated by LDA (2.52 mmol) in THF (15 mL) at −70 °C and treated with cyclopent-2-enone (207 mg, 2.52 mmol) in THF (2 mL) at −70 °C. After 5 min, the reaction mixture was cooled to ca. −90 °C and then an aliquot (5 mL) was withdrawn via syringe and discharged rapidly into aqueous ammonium chloride. The oil obtained on workup was shown by TLC to comprise the conjugate and carbonyl adducts. The remainder of the reaction mixture was warmed to −10 °C and was quenched with aqueous ammonium chloride solution. Workup gave an oil shown by TLC and ^1H NMR spectroscopy to be essentially free of the carbonyl adducts **13a,b**.

The carbonyl adduct **13a,b** (159 mg, 0.61 mmol) in THF (15 mL) was cooled to −70 °C, and a solution of LDA (0.73 mmol in THF, 5 mL) was added dropwise, inducing a color change to yellow. The resultant solution was warmed to −10 °C during 15 min and quenched with aqueous ammonium chloride solution. The usual workup gave a yellow oil (141 mg), which contained 2-methyl-1-(phenylsulfinyl)prop-2-ene, the carbonyl adducts **13a,b**, and the conjugate adducts **11a,b** and **12a,b** in a ratio of 40:20:20:20 as shown by ^1H NMR spectroscopy (90 MHz). Each component was separated by flash chromatography with 20:80 ethyl acetate–diethyl ether to enable identification to be made by comparison with authentic samples.

3-[(1,1-Dimethylethyl)sulfinyl]-2-methylprop-1-ene (2). From the sulfoxide (264 mg, 1.645 mmol) and cyclopent-2-enone (135 mg, 1.645 mmol) at −70 °C was obtained after quenching of the reaction mixture with saturated aqueous ammonium chloride a pale yellow oil (365 mg). This was submitted to flash chromatography with ethyl acetate and then 4:96 methanol–ethyl acetate to give a 94:6 mixture of the E and Z isomers **14a,b** and **15a,b** of *3-[3'-[(1,1-dimethylethyl)sulfinyl]-2'-methylprop-2-enyl]cyclopentanone* as a colorless viscous oil (270 mg, 68%). The E isomer **14a,b** was a 59:41 and the Z isomer **15a,b** a 1:1 mixture of diastereomers. Attempts to separate the E and Z isomers by HPLC were unsuccessful: IR (neat) ν_{max} 3000–2840 (s), 2710 (sh), 1732 (s), 1625 (m), 1460 (m), 1440 (sh), 1402 (m), 1380 (m), 1362 (m), 1240 (w), 1160 (s), 1139 (sh), 1035 (s), 1015 (s), 928 (m), 790 (m), 752 (s), 730 (s) cm^{-1}; ^1H NMR [* denotes minor E diastereomer **14b**] δ 1.236*, 1.245 (9 H, s, t-Bu, E), 1.241, 1.247 (9 H, s, t-Bu, Z), 1.496–1.658 (1 H, m, H3), 1.776–1.902 (1 H, m, H2β), 1.973*, 1.976 (3 H, d, J = 1.2 Hz, CH_3, Z), 1.992*, 2.00 (3 H, d, J = 1.2 Hz, CH_3, E), 2.10–2.56 (7 H, m, H2α, H4, H5, H1'), 5.857 (1 H, br s, $w_{h/2}$ = 2.4 Hz, H3', E), 5.980, 6.004 (1 H, br s, $w_{h/2}$ = 2.4 Hz, H3', Z); MS (CI) m/e 243 (M + 1, 100), 225 (8), 169 (24), 157 (7), 135 (12), 111 (7), 86 (8), 83 (8), 57 (14), 41 (7), 29 (22). Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.4; H, 9.15. Found: C, 64.4; H, 9.3.

The sulfoxide (275 mg, 1.72 mmol) was deprotonated at −15 °C and treated with cyclopent-2-enone (141 mg, 1.72 mmol) at −10 °C to give after flash chromatography according to the above conditions a 66:34 mixture of the products **14a,b** and **15a,b** (302 mg, 73%). Each geometric isomer consisted of 58:42 and 77:23 mixtures of diastereomers **a** and **b** as indicated by integration of the *tert*-butyl resonances in the ^1H NMR spectrum at δ 1.236, 1.241, 1.244, and 1.247.

The sulfoxide (201 mg, 1.254 mmol) was deprotonated at −70 °C and was treated at −10 °C with cyclopent-2-enone (113 mg, 1.38 mmol) to give a viscous pale yellow oil (253 mg, 83%) whose ^1H NMR spectrum indicated that it was a 73:27 mixture of the products **14a,b** and **15a,b**.

(E)-1-[(1,1-Dimethylethyl)sulfinyl]-2-methylbut-2-ene (3). The sulfoxide (195 mg, 1.12 mmol) and cyclopent-2-enone (101 mg, 1.23 mmol) at −70 °C gave after flash chromatography with 1:99 methanol–ethyl acetate the diastereomers **16a,b** and **17a,b** of *3-[3'-[(1,1-dimethylethyl)sulfinyl]-1',2'-dimethylprop-2'-enyl]cyclopentanone* (240 mg, 84%) in an overall ratio of 55:29:11:5 as a colorless viscous oil: IR (neat) ν_{max} 2950 (s), 2925–2865 (s), 1739 (s), 1622 (m), 1460 (s), 1440 (w), 1408 (m), 1385 (m), 1367 (m), 1287 (w), 1165 (s), 1100 (m), 1038 (s), 930 (m), 820 (m), 735 (s) cm^{-1}; ^1H NMR (**16a**) δ 1.176 (3 H, d, J = 6.3 Hz, 1'-CH_3), 1.232 (9 H, s, t-Bu), 1.475–1.599 (1 H, m, H4β), 1.937 (3 H, d, $J \simeq$ 1 Hz, 2'-CH_3), 1.67–2.50 (7 H, m, H2, H3, H4α, H5, H1'), 5.858 (1 H, br s, $w_{h/2}$ = 3.2 Hz, H3'), 5.934 (1 H, q, J = 1.2 Hz, H3'); ^1H NMR (**16b**) δ 1.128 (3 H, d, J = 6.3 Hz, 1'-CH_3), 1.243 (9 H, s, t-Bu), 1.959 (3 H, d, $J \simeq$ 1 Hz, 2'-CH_3), 5.899 (1 H, br s, $w_{h/2}$ = 3.2 Hz, H3'); ^1H NMR (**17a**) δ 1.077 (3 H, d, J = 7.2 Hz, 1'-CH_3), 1.899 (3 H, d, $J \simeq$ 1 Hz, 2'-CH_3), 5.934 (1 H, q, J = 1.2 Hz, H3'); ^1H NMR (**17b**) δ 1.119 (3 H, d, J = 7.2 Hz, 1'-CH_3), 1.863 (3 H, d, $J \simeq$ 1 Hz, 2'-CH_3), 5.869 (1 H, q, J = 1.2 Hz, H3'); MS (CI) m/e 257 (M + 1, 100), 183 (36), 149 (22), 125 (26), 100 (20), 57 (26), 29 (31). Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.6; H, 9.4. Found: C, 65.0; H, 9.5.

From the sulfoxide (238 mg, 1.37 mmol) and cyclopent-2-enone (112 mg, 1.37 mmol) at −10 °C was obtained after flash chromatography with ethyl acetate and then 4:96 methanol–ethyl acetate the conjugate adducts **16a,b** and **17a,b** (231 mg, 66%) as a colorless viscous oil in an overall ratio of 38:34:19:9. The mixture (149 mg, 0.58 mmol) in dichloromethane (15 mL) was treated with *m*-chloroperoxybenzoic acid (120 mg, 0.70 mmol) in dichloromethane (5 mL). After 2 h, diethyl ether was added and the organic phase was washed with potassium carbonate and brine solutions and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure left a pale viscous oil, which was submitted to flash chromatography with 1:1 ethyl acetate–light petroleum to give *3-[3'-[(1,1-dimethylethyl)sulfonyl]-1',2'-dimethylprop-2'-enyl]cyclopentanone* (130 mg, 82%) as mixture of diastereomers in an overall ratio of 36:34:21:9 as a colorless viscous oil. The first two diastereomers possessed E geometry at the double bond, the second two, Z geometry: IR ($CHCl_3$) ν_{max} 2950 (s), 1735 (s), 1617 (s), 1457 (m), 1399 (m), 1330 (w), 1284 (s), 1158 (s), 1111 (s), 970 (w), 859 (m), 821 (m) cm^{-1}; ^1H NMR (major E isomer) δ 1.201 (3 H, d, J = 6.4 Hz, 1'-CH_3), 1.364 (9 H, s, t-Bu), 1.424–1.607 (1 H, m, H3), 2.125 (3 H, d, J = 1.2 Hz, 2'-CH_3), 1.74–2.52 (7 H, m, H2, H4, H5, H1'), 6.05 (1 H, q, J = 1.4 Hz, H3');

^{1}H NMR (minor *E* isomer) δ 1.159 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.384 (9 H, s, *t*-Bu), 2.167 (3 H, d, *J* = 1.2 Hz, 2′-CH_3), 6.012 (1 H, q, *J* = 1.4 Hz, H3′); ^{1}H NMR (major *Z* isomer) δ 1.106 (3 H, d, *J* = 6.8 Hz, 1′-CH_3), 1.386 (9 H, s, *t*-Bu), 1.943 (3 H, d, *J* = 1.2 Hz, 2′-CH_3), 5.995 (1 H, q, *J* = 1.4 Hz, H3′); ^{1}H NMR (minor *Z* isomer) δ 1.157 (3 H, d, *J* = 6.8 Hz, 1′-CH_3), 1.374 (9 H, s, *t*-Bu), 1.902 (3 H, d, *J* = 1.2 Hz, 2′-CH_3), ca. 6.01 (1 H, q, *J* = 1.4 Hz, H3′); MS (CI) *m/e* 545 (2M + 1, 49), 273 (M + 1, 100), 199 (28), 181 (37), 83 (21), 57 (36). Anal. Calcd for $C_{14}H_{24}O_4S$: C, 61.7; H, 8.9. Found: C, 62.0; H, 8.5.

(*Z*)-1-[(1,1-Dimethylethyl)sulfinyl]-2-methylbut-2-ene (4). From the sulfoxide (282 mg, 1.62 mmol) and cyclopent-2-enone (133 mg, 1.62 mmol) at −70 °C was obtained after flash chromatography with 4:96 methanol–ethyl acetate a 93:7 mixture of the diastereomers **18a** and **18b** of the conjugate addition product as a colorless, viscous oil (251 g, 61%). A solution of the oil in light petroleum–dichloromethane deposited prisms, mp 94–96 °C, of *(1′RS,2′E,3SR,SSRS)-3-[3′-[(1,1-dimethylethyl)sulfinyl]-1′,2′-dimethylprop-2′-enyl]cyclopentanone* (**18a**): IR ($CHCl_3$) ν_{max} 2950 (s), 2455 (m), 1730 (s), 1625 (m), 1452 (s), 1400 (m), 1380 (m), 1332 (m), 1238–1200 (s), 1160 (s), 1090 (m), 1015 (s), 998 (s), 859 (w), 810–640 (s) cm^{-1}; ^{1}H NMR δ 1.183 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.23 (9 H, s, *t*-Bu), 1.478–1.598 (1 H, m, H3), 1.70–1.830 (1 H, m, H4), 1.904 (3 H, d, *J* ≃ 1 Hz, 2′-CH_3), 2.134–2.334 (1 H, m, H4), 2.378 (1 H, dd, *J* = 18, 8.5 Hz, H2β), 5.857 (1 H, q, *J* = 1.1 Hz, H3′); MS (CI) *m/e* 257 (M + 1, 100), 200 (23), 183 (35), 117 (55), 101 (30), 100 (100), 83 (42), 57 (82), 55 (24), 41 (29), 29 (100), 27 (33). Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.6; H, 9.4. Found: C, 65.3; H, 9.7. The minor isomer **18b** could not be obtained free of the major isomer: ^{1}H NMR δ 1.174 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.938 (3 H, d, *J* ≃ 1 Hz, 2′-CH_3), 5.896 (1 H, br s, $w_{h/2}$ = 4.2 Hz, H3′).

The crude product obtained from the above reaction (64.7 mg, 0.252 mmol) in dichloromethane (8 mL) was treated with *m*-chloroperoxybenzoic acid (47.9 mg, 0.278 mmol) in dichloromethane (2 mL) as previously described to give the crude sulfone (74 mg). This was chromatographed with 1:1 ethyl acetate–light petroleum to give a 95:5 mixture of diastereomers of the sulfone as a white solid (61.5 mg, 90%). This gave *(1′RS,2′E,3SR)-3-[3′-[(1,1-dimethylethyl)sulfonyl]-1′,2′-dimethylprop-2′-enyl]cyclopentanone* as prisms, mp 95–97 °C, from ether: IR ($CHCl_3$) ν_{max} 2955 (s), 2875 (m), 1730 (s), 1615 (s), 1452 (m), 1400 (m), 1282 (s), 1230–1200 (m), 1160 (m), 1110 (s), 1010 (w), 972 (w), 860 (m), 821–650 (s) cm^{-1}; ^{1}H NMR δ 1.201 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.361 (9 H, s, *t*-Bu), 1.483–1.603 (1 H, m, H3), 1.798 (1 H, m, H4), 2.125 (3 H, d, *J* = 1.2 Hz), 2.146–2.339 (5 H, m, H2α, H4, H5, H1′), 2.378 (1 H, dd, *J* = 17.2, 8.8 Hz, H2β), 6.015 (1 H, q, *J* = 1.2 Hz, H3); MS (CI) *m/e* 273 (M + 1, 13), 217 (8), 199 (20), 181 (20), 83 (23), 57 (20), 41 (18), 29 (100). Anal. Calcd for $C_{14}H_{24}O_3S$: C, 61.7; H, 8.9. Found: C, 61.9; H, 8.9. The minor isomer could not be obtained free of the major isomer: ^{1}H NMR δ 1.159 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.381 (9 H, s, *t*-Bu), 2.161 (3 H, d, *J* = 1.2 Hz), 6.050 (1 H, br s, $w_{h/2}$ = 3.6 Hz, H3).

(*E*)-(2-Methylbut-2-enyl)diphenylphosphine oxide (5). The phosphine oxide (261 mg, 0.97 mmol) in THF (15 mL) at −70 °C under nitrogen was treated with butyllithium until the first permanent orange color of the anion appeared; 1 equiv (0.49 mL, 0.97 mmol, 1.96 M in hexane) was then added. After 5 min, cyclopent-2-enone (87 mg, 1.06 mmol) in THF (2 mL) was added dropwise; during the addition the color of the anion disappeared. After a further 5 min, the reaction mixture was quenched with saturated ammonium chloride solution (10 mL). The usual workup followed by flash chromatography with 2:98 methanol–ethyl acetate gave a 93:7 mixture of the diastereomers **19a** and **19b** as a glass (268 mg, 79%), which slowly crystallized. Trituration of the solid with ether afforded *(1′RS,2′E,3RS)-3-[3′-(diphenylphosphinoyl)-1′,2′-dimethylprop-2′-enyl]cyclopentanone* (**19a**) as small prisms: mp 120–122 °C; IR ($CHCl_3$) ν_{max} 2973 (s), 1975 (w), 1738 (s), 1618 (s), 1467 (w), 1438 (m), 1383 (w), 1172 (s), 1119 (m), 1105 (m), 750 (m) cm^{-1}; ^{1}H NMR δ 1.141 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.517 (1 H, dddd, *J* = 12.2, 11.1, 9.7, 7.8 Hz, H4β), 1.843 (1 H, ddd, *J* = 18.2, 10.5, 1.4 Hz, H2β), 2.02–2.07 (1 H, m, H3), 2.050 (3 H, dd, *J* = 2.7, 0.9 Hz, 2′-CH_3), 2.160 (1 H, dddd, *J* = 18.3, 11.4, 8.4, 1.3 Hz, H5α), 2.17–2.25 (2 H, m, H1′, H4α), 2.326 (1 H, dddd, *J* = 18.4, 8.1, 1.9, 1.4 Hz, H5β), 2.445 (1 H, ddd, *J* = 18.2, 6.2, 1.3 Hz, H2α), 5.974 (1 H, dq, *J* = 25.0, 0.9 Hz, H3′), 7.43–7.77 (10 H, m, C_6H_5); preirradiation at δ 1.141 (1′-CH_3) resulted in enhancements at δ 2.05 (2′-CH_3) of 0.8% and at δ 2.25 (H1′) of 2.5%, preirradiation at δ 2.050 (2′-CH_3) resulted in enhancements at δ 1.14 (1′-CH_3) of 0.9% and at δ 1.52 (H4β) of 3%; MS *m/e* 352 (M, 1), 270 (40), 202 (100), 201 (34), 77 (15), 55 (10), 47 (14), 32 (23), 28 (100). Anal. Calcd for $C_{22}H_{25}O_2P$: C, 75.0; H, 7.15. Found: C, 74.8; H, 7.3. The minor isomer could not be obtained free of the major isomer. Its characterization is described below.

(*Z*)-(2-Methylbut-2-enyl)diphenylphosphine Oxide (6). From the phosphine oxide (249 mg, 0.92 mmol) and cyclopent-2-enone (83 mg, 1.01 mmol) at −70 °C according to the foregoing conditions was obtained after flash chromatography a 95:5 mixture of the diastereomers **19b** and **19a** as a colorless highly viscous oil (245 mg, 76%). The major isomer **19b** was *(1′RS,2′E,3SR)-3-[3′-(diphenylphosphinoyl)-1′,2′-dimethylprop-2′-enyl]cyclopentanone*: IR (neat) ν_{max} 3056 (m), 2967 (s), 2932 (s), 2894 (s), 2877 (s), 1738 (s), 1614 (s), 1454 (m), 1438 (s), 1402 (m), 1183 (s), 1162 (s), 1117 (s), 1102 (s), 820 (m), 745 (s), 718 (s), 697 (s) cm^{-1}; ^{1}H NMR δ 1.179 (3 H, d, *J* = 6.4 Hz, 1′-CH_3), 1.46–1.57 (1 H, m, H4β), 1.836 (1 H, ddd, *J* = 17.5, 9.4, 1.4 Hz, H2β), 2.009 (3 H, dd, *J* = 2.6, 0.9 Hz, 2′-CH_3), 2.12–2.32 (5 H, m, H1′, H2α, H3, H4α, H5α), 2.348 (1 H, ddd, *J* = 17.3, 7.2, <1 Hz, H5β), 5.935 (1 H, dq, *J* = 25, 1.0 Hz, H3′), 7.42–7.76 (10 H, m, C_6H_5); MS *m/e* 352 (M, 2), 270 (41), 202 (100), 201 (50), 125 (15), 77 (28), 47 (24), 43 (16), 32 (35), 28 (100); HRMS calcd for $C_{22}H_{25}O_2P$ 352.1592, found 352.1600. The minor isomer could not be separated from the major isomer. Its characterization is described above.

2-Methyl-4-(phenylsulfinyl)pent-2-ene (7a,b). The sulfoxide (422 mg, 2.03 mmol) and cyclopent-2-enone (166 mg, 2.03 mmol) at −70 °C gave after flash chromatography with 45:55 ethyl acetate–light petroleum a 1:1 mixture of the products **20** and **21a** as a pale yellow oil (490 mg, 83%). The mixture was submitted to HPLC with 40:60 ethyl acetate–light petroleum (Waters semipreparative μ-Porasil No. 2 column, flow-rate 3 mL min^{-1}, 1000 psi) to give first *(2′E,3RS,RSSS)-3-[1′,1′-dimethyl-3′-(phenylsulfinyl)but-2′-enyl]cyclopentan-1-one* (**20**) as an amorphous solid: mp 58–60 °C; IR (neat) ν_{max} 2960 (s), 1740 (s), 1480 (m), 1440 (m), 1410 (m), 1380 (m), 1170 (m), 1050 (s) cm^{-1}; ^{1}H NMR δ 1.185 (3 H, s, CH_3), 1.195 (3 H, s, CH_3), 1.59–1.74 (1 H, m, H4β), 1.92–2.42 (6 H, m, H2, H3α, H4α, H5), 1.746 (3 H, d, *J* = 1.4 Hz, H4′), 6.419 (1 H, q, *J* = 1.4 Hz, H2′), 7.47–7.60 (5 H, m, C_6H_5); preirradiations at δ 6.419 (H2′) and 1.746 (H4′) did not induce any enhancements at δ 1.72 and 6.39, respectively; MS *m/e* 290 (M^+, 4), 207 (8), 166 (10), 165 (80), 191 (20), 126 (60), 123 (250), 83 (55), 82 (15), 81 (78), 55 (100). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.3; H, 7.6. Found: C, 70.4; H, 7.7.

The next isomer to be eluted was *(2′Z,3RS,SSRS)-3-[1′,1′-dimethyl-3′-(phenylsulfinyl)but-2′-enyl]cyclopentanone* (**21a**) as prisms, mp 169.5–171 °C from ethyl acetate–light petroleum: IR (neat) ν_{max} 2960 (s), 1740 (s), 1480 (w), 1440 (m), 1410 (m), 1380 (m), 1080 (m), 1050 (s) cm^{-1}; ^{1}H NMR δ 1.375 (3 H, s, CH_3), 1.446 (3 H, s, CH_3), 1.68–1.80 (1 H, m, H4β), 2.01–2.47 (6 H, m, H2, H3α, H4α, H5), 1.702 (3 H, d, *J* = 1.3 Hz, H4′), 6.026 (1 H, q, *J* = 1.3 Hz, H2′), 7.45–7.65 (5 H, m, C_6H_5); preirradiation at δ 1.702 (H4′) induced enhancement (6%) at δ 6.026 (H2′), preirradiation at δ 6.026 induced enhancement (7%) at δ 1.702; MS *m/e* 274 (M^+ − O, 20), 273 (100), 191 (52), 126 (28), 123 (28), 109 (38), 83 (55), 81 (53), 55 (100). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.3f H, 7.6. Found: C, 70.4; H, 7.7.

Similar results were obtained when the lithiated sulfoxide was generated at −70 °C, treated with cyclopentenone at −17 °C, and quenched at −10 °C.

A solution of tributylphosphine (372 mg, 1.86 mmol) and HMPA (333 mg, 1.86 mmol) in dry diethyl ether (15 mL) at room temperature under nitrogen was treated with a solution of iodine (230 mg, 1.8 mmol) in ether (5 mL). The resultant white suspension was treated with a solution of the mixture of the conjugate addition products **20** and **21a** (539 mg, 1.86 mmol) in diethyl ether (5 mL). During the reduction, the mixture became a clear yellow solution. This was quenched with water and extracted with diethyl ether. The extracts were washed with water and brine and then dried (Na_2SO_4) and evaporated under reduced pressure to leave a yellow oil, which upon flash chromatography with 40:60 ethyl acetate–light petroleum ether gave first *(E)-3-[1′,1′-trimethyl-3′-(phenylthio)but-2′-enyl]cyclopentanone* (**22**; 210 mg, 42%) as a colorless oil: IR (neat) ν_{max} 2960 (s), 1740 (s), 1660 (w), 1580 (w), 1480 (m), 1440 (w), 1370 (w), 1170 (m) cm^{-1}; ^{1}H NMR δ 1.15 (6 H, s, 2 CH_3), 2.02 (3 H, d, *J* = 1.2 Hz, H4′), 1.8–2.4 (7 H, m, H2, H3, H4, H5), 5.79 (1 H, q, *J* = 1.2 Hz, H2′), 7.2–7.3 (5 H, m, C_6H_5); MS *m/e* 274 (M^+, 5), 192 (20), 191 (100), 149 (10). Anal. Calcd for $C_{17}H_{22}OS$: C, 74.4; H, 8.0; S, 11.7. Found: C, 74.0; H, 8.4; S, 11.5.

The next compound eluted was *(Z)-3-[1′,1′-dimethyl-3′-(phenylthio)but-2′-enyl]cyclopentanone* (**23**) as a colorless oil (210 mg, 42%): IR (neat) ν_{max} 2960 (s), 1740 (s), 1590 (m), 1490 (m), 1440 (m), 1410 (w), 1160 (m) cm^{-1}; ^{1}H NMR δ 1.28 (6 H, s, 2 CH_3), 1.84 (3 H, d, *J* = 1.2 Hz, H4), 2.0–2.6 (7 H, m, H2, H3, H4, H5), 5.70 (1 H, q, *J* = 1.2 Hz, H2′), 7.15–7.30 (5 H, m, C_6H_5); MS *m/e* 274 (M^+, 5), 192 (20), 191 (100), 149 (10), 81 (13); HRMS calcd for $C_{17}H_{22}OS$, 274.1391, found 274.1383.

Cyclopent-2-enone (234 mg, 2.85 mmol) in THF (2 mL) was added to lithiated 3-methyl-1-(phenylsulfinyl)but-2-ene (from the sulfoxide **24**,[1] 512 mg, 2.64 mmol, and LDA, 2.75 mmol) in THF (35 mL) under nitrogen at −70 °C. The resultant solution was treated at −70 °C with butyllithium (1.6 mL, 1.8 M in hexanes, 2.8 mmol) to produce a dark

grey black solution. Methyl iodide (0.33 mL, 5.28 mmol) in THF (5 mL) was then added dropwise; during the addition the color of the solution became pale yellow. After 5 min, the solution was quenched with aqueous ammonium chloride and worked up in the usual fashion to give after flash chromatography with 40:60 ethyl acetate–light petroleum ether a colorless oil (640 mg, 83%), ^{1}H NMR analysis of which indicated that it consisted of 93:7 mixture of the (*E*)-sulfoxide **20** and the (*Z*)-sulfoxide **21b**, whose characterization is described below.

A mixture of the sulfoxides **20** and **21a** (1:1; 206 mg, 0.71 mmol) in THF (2 mL) was added to LDA (1.8 mmol) in THF (30 mL) at −70 °C under nitrogen. The solution was stirred for 5 min and was thereupon worked up to give a yellow oil (190 mg) consisting of the (*Z*)-sulfoxides **21a** and **21b**, the allene **26**, and (phenylthio)benzenesulfonate. The latter were separated from the sulfoxides by flash chromatography and then submitted to HPLC with 3:97 ethyl acetate–light petroleum ether to give *3-(1′,1′-dimethylbuta-2′,3′-*dienyl)*cyclopentanone* (**26**) as a colorless oil: IR (neat) ν_{max} 3150 (w), 2950 (s), 1950 (s), 1750 (s), 1480 (m), 1460 (s), 1400 (m), 1380 (m), 1340 (m), 1180 (s), 1160 (s), 1120 (m), 1080 (w), 870 (s), 650 (s) cm^{-1}; ^{1}H NMR δ 1.05 (3 H, s, CH_3), 1.07 (3 H, s, CH_3), 1.5–2.5 (7 H, m, H2, H3, H4, H5), 4.76 (2 H, d, H4′), 5.07 (1 H, dd, $J \simeq 6.6, 6.6$ Hz, H2′); MS *m/e* 164 (M^+, 3), 163 (30), 83 (10), 82 (20), 81 (100). The amount of allene formed depended upon the amount of LDA used; in the above case, it constituted approximately 70% of the reaction mixture.

The mixture of sulfoxides **20** and **21a** (1:1; 620 mg, 2.14 mmol) in THF (5 mL) was added to a solution of LDA (2.35 mmol) in THF (40 mL) at −70 °C under nitrogen. The resultant solution was stirred for 5 min and was then quenched and worked up in the usual manner to give a pale yellow oil (570 mg), consisting of a 3:2 mixture of the sulfoxides **21a** and **21b**, the allene **26**, and (phenylthio)benzenesulfonate. The other products were separated from the sulfoxide isomers by flash chromatography, and the isomers were then separated by HPLC with 30:70 ethyl acetate–light petroleum ether according to the above conditions to give first the isomerized sulfoxide **21b**, as prisms, mp 89–90.5 °C from ethyl acetate–light petroleum: ^{1}H NMR δ 1.373 (3 H, s, CH_3), 1.452 (3 H, s, CH_3), 1.691 (3 H, d, J = 1.4 Hz, H4′), 1.72–2.62 (7 H, m, H2, H3, H4, H5), 6.146 (1 H, q, J = 1.3 Hz, H2′); 7.43–7.61 (5 H, m, C_6H_5); preirradiation at δ 6.146 (H2′) induced enhancement at 1.691 (H4′) of 9%, preirradiation at δ 1.691 induced enhancement at 6.146 of 3%; MS *m/e* 395 (20), 393 (60), 391 (58), 373 (6), 357 (292, M + 1, 20), 267 (8), 265 (10), 193 (15), 191 (55), 175 (12), 163 (18), 126 (100), 109 (80), 83 (80), 77 (52); HRMS calcd for $C_{17}H_{22}O_2S$ 291.11418 (M + 1), found 291.1393.

4-[(1,1-Dimethylethyl)sulfinyl]-2-methylpent-2-ene (8a,b). The sulfoxide (443 mg, 2.36 mmol) and cyclopent-2-enone (208 mg, 2.5 mmol) at −15 °C gave after flash chromatography with 40:60 ethyl acetate–light petroleum (*2′E,3RS,S$_S$R$_S$)-3-[3′-[(1,1-dimethylethyl)sulfinyl]-1′,1′-dimethylbut-2′-enyl]cyclopentan-1-one* (**27**; 550 mg, 83%) as a colorless oil: IR (neat) ν_{max} 2960 (s), 1740 (s), 1470 (m), 1360 (m), 1160 (m), 1045 (s) cm^{-1}; ^{1}H NMR δ 1.194 (9 H, s, *t*-Bu), 1.220 (3 H, s, CH_3), 1.246 (3 H, s, CH_3), 1.59–1.73 (1 H, m, H4β), 1.95–2.41 (6 H, m, H2, H3α, H4α, H5), 1.985 (3 H, d, J = 1.5 Hz, H4′), 5.980 (1 H, q, J = 1.5 Hz, H2′); preirradiation at δ 5.98 (H2′) and at δ 1.985 (H4′) did not induce enhancements of the complementary signals; MS (CI) *m/e* 270 (P), 541 (2P + 1). Anal. Calcd for $C_{15}H_{20}O_2S$: C, 66.7; H, 9.6. Found: C, 66.7; H, 9.7.

3-[(1,1-Dimethylethyl)sulfinyl]cyclopent-1-ene (9a,b). The less polar of the two sulfoxides, **9a** (529 mg, 3.08 mmol), and cyclopentenone (277 mg, 3.37 mmol) at −70 °C gave after flash chromatography with 35:65 ethyl acetate–light petroleum (*1′RS,3SR,S$_S$R$_S$)-3-[3′-[(1,1-dimethyl)sulfinyl]cyclopent-2′-enyl]cyclopentanone* (**28**; 313 mg, 40%) as colorless needles, mp 108–109 °C, from acetone–light petroleum: IR ($CHCl_3$) ν_{max} 2960 (s), 1740 (s), 1460 (m), 1400 (m), 1360 (m), 1240 (m), 1160 (m), 1030 (s) cm^{-1}; ^{1}H NMR δ 1.25 (9 H, s, *t*-Bu), 1.55–2.90 (12 H, m), 6.30 (1 H, dd, J = 3.8, 1.8 Hz, H2′); MS (CI) *m/e* 255 (P + 1), 509 (2P + 1). Anal. Calcd for $C_{14}H_{22}O_2S$: C, 66.1; H, 8.7; S, 12.6. Found: C, 66.5; H, 8.4; S, 12.5.

Also isolated by flash chromatography of the reaction mixture in variable yields (to 40%) was a nonpolar, unstable light yellow oil, which rapidly darkened. This was tentatively identified as *3-(1′-hydroxycyclopent-2′-enyl)cyclopent-2-enyl (1,1-dimethylethyl)sulfinate* (**29**): IR (neat) ν_{max} 3400 (s), 2950 (s), 2880 (sh), 1640 (w), 1460 (s), 1370 (s), 1340 (s), 1170 (s), 1050 (s), 1030 (s), 940 (m), 880 (m), 830 (m) cm^{-1}; ^{1}H NMR δ 1.4 (9 H, s, *t*-Bu), 1.7–2.7 (9 H, m), 4.8 (br s, $w_{h/2}$ = 27 Hz, OH), 5.6–6.1 (3 H, m, H2, H2′, H3′); MS *m/e* 280 (3), 278 (1.5), 260 (1.5), 205 (2), 170 (6), 149 (20), 148 (32), 129 (76).

The more polar diastereomer of the starting sulfoxide (405 mg, 2.35 mmol) and cyclopentenone (212 mg, 2.59 mmol) at −70 °C gave the above products **28** and **29** in the same yields.

Cyclopent-2-enyldiphenylphosphine Oxide (10). From the phosphine oxide (622 mg, 2.32 mmol) and cyclopent-2-enone (210 mg, 2.32 mmol) at −70 °C was obtained after flash chromatography with 65:35 ethyl acetate–light petroleum (*1′RS,3SR)-3-[3′-(diphenylphosphinoyl)cyclopent-2′-enyl]cyclopentanone* (**30**; 630 mg, 79%) as a colorless viscous liquid: IR (neat) ν_{max} 2950 (s), 1740 (s), 1600 (w), 1440 (s), 1410 (m), 1320 (m), 1190 (s), 1120 (s), 790 (m), 720 (m), 690 (m) cm^{-1}; ^{1}H NMR δ 1.51–2.94 (12 H, m), 6.53 (1 H, ddd, J = 10.3, 3.6, 1.7 Hz, H2′), 7.39–7.78 (10 H, m, C_6H_5); MS *m/e* 350 (13), 284 (10), 283 (40), 282 (30), 268 (63), 267 (60), 202 (60), 201 (100), 185 (58), 183 (32); HRMS calcd for $C_{22}H_{23}O_2P$ 350.1435, found 350.1440.

Quenching Experiments. The less polar cyclopentenyl sulfoxide **9a** (515 mg, 2.99 mmol) in THF (5 mL) was added to LDA (3.29 mmol) in THF (30 mL) at −70 °C under nitrogen. The resultant solution was stirred for 5 min and then treated with saturated aqueous ammonium chloride at −70 °C. Workup according to the method used for the conjugate addition reactions[1] left a brown oil (468 mg, 91%). This was assayed by ^{1}H NMR spectroscopy and by analytical HPLC (ethyl acetate–light petroleum, 35:65, Brownlee SI 100 4.6 mm i.d. × 25 cm 5-μm column, flow rate 5 mL min^{-1}, 700 psi) and shown to consist of the more polar isomer **9b**. The less polar isomer **9a** could not be detected in the crude reaction mixture. Treatment of the more polar cyclopentenyl sulfoxide **9b** (335 mg, 1.94 mmol) with LDA (2.14 mmol) in THF according to the above conditions gave a brown oil (311 mg, 93%), which was shown to consist of the cyclopentenyl sulfoxide **9b**. The less polar isomer **9a** could not be detected in the crude reaction mixture.

Acknowledgment. We express our gratitude to the Australian Research Grants Committee for financial support of this work. We thank Dr. Jacques Nemorin and Dr. Bruce Rowe for their care and expertise in conducting the numerous ^{1}H NMR NOE difference experiments required in this work.

Registry No. 1, 43161-07-5; **2**, 114652-37-8; **2** sulfide, 94514-04-2; **3**, 114652-38-9; **3** sulfide, 114652-46-9; **4**, 114652-39-0; **4** sulfide, 114652-47-0; **5**, 57984-58-4; **6**, 57984-57-3; **7** (isomer 1), 114652-40-3; **7** (isomer 2), 114652-43-6; **7** sulfide, 21213-20-7; **8** (isomer 1), 114652-41-4; **8** (isomer 2), 114652-44-7; **8** sulfide, 91009-86-8; **9** sulfide, 114652-48-1; **9a**, 114652-42-5; **9b**, 114652-45-8; **10**, 54807-91-9; **11** (isomer 1), 114652-49-2; **11** (isomer 2), 114652-50-5; **12** (isomer 1), 114652-53-8; **12** (isomer 2), 114652-54-9; **13** (isomer 1), 114652-51-6; **13** (isomer 2), 114652-52-7; **14** (isomer 1), 114652-55-0; **14** (isomer 2), 114652-56-1; **15** (isomer 1), 114652-57-2; **15** (isomer 2), 114652-58-3; **16a**, 114716-28-8; **16a** sulfone, 114652-59-4; **16b**, 114716-29-9; **16b** sulfone, 114652-60-7; **17a**, 114716-30-2; **17a** sulfone, 114652-61-8; **17b**, 114716-31-3; **17b** sulfone, 114652-62-9; **18a**, 114716-32-4; **18b**, 114716-33-5; **19a**, 114652-63-0; **19b**, 114652-64-1; **20**, 114652-65-2; **21a**, 114652-66-3; **21b**, 114652-68-5; **22**, 114652-67-4; **23**, 114674-39-4; **24**, 42185-88-6; **26**, 114674-40-7; **27**, 114652-69-6; **28**, 114652-70-9; **29**, 114652-71-0; **30**, 114652-72-1; 2-methyl-1-(phenylthio)prop-2-ene, 702-00-1; (*E*)-2-methylbut-2-en-1-ol, 497-02-9; (*E*)-1-bromo-2-methylbut-2-ene, 57253-30-2; (*Z*)-2-methylbut-2-en-1-ol, 19319-26-7; (*Z*)-1-bromo-2-methylbut-2-ene, 57253-29-9; 4-bromo-2-methylpent-2-ene, 4325-84-2; 3-chloro-2-methylprop-1-ene, 563-47-3; sodium 2-methylpropane-2-thiolate, 29364-29-2; sodium benzenethiolate, 930-69-8; 4-methylpent-3-en-2-ol, 4325-82-0; benzenethiol, 108-98-5; 2-methylpropane-2-thiol, 75-66-1; 3-chlorocyclopent-1-ene, 96-40-2; diphenylphosphine, 829-85-6; cyclopent-2-enone, 930-30-3.

Supplementary Material Available: Crystallographic data, tables of positional parameters, bond lengths, bond angles, and thermal parameters, and ORTEP drawings for **18a** and **28** (10 pages). Ordering information is given on any current masthead page.