possibly be scavenged by the solvent or undergo radical recombination reactions whereas the $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ species may undergo disproportionation to give $[Pt_2(pop)_4]^{4-}$ and $[Pt_2(pop)_4X_2]^{4-}$ as suggested by previous work.[20,21,24] From Table II, the ϕ_r values for $[Pt_2(pop)_4X_2]^{4-}$ depend on the nature of axial ligands and decrease with $X_2 = (CH_3)(I) > (SCN)_2 > I_2 > Im_2 > Cl_2 > Br_2$. With the exception of $[Pt_2(pop)_4Cl_2]^{4-}$, this trend parallels the corresponding decrease in Pt-Pt bond distances [X_2, d(Pt-Pt) in angstroms: $(CH_3)(I)$, 2.78 (1); $(SCN)_2$, 2.760 (1); I_2, 2.754 (1); Im_2, 2.745 (1); Br_2, 2.723 (4); Cl_2, 2.695 (1)].[6,25-28]

Such a correlation of ϕ_r values with d(Pt-Pt) bond distances is not unreasonable given the fact that the photoreaction

$$[Pt_2(pop)_4X_2]^{4-} \xrightarrow{h\nu} [Pt_2(pop)_4]^{4-}$$

involves breakage of the metal-metal bond. The reactive $[Pt^{II}Pt^{III}(pop)_4X]^{4-}$ intermediate and $[Pt_2(pop)_4]^{4-}$ products with $(d_\sigma)^2(d_\sigma^*)^1$ and $(d_\sigma)^2(d_\sigma^*)^2$ configurations, respectively, should have weaker Pt-Pt bond strengths than the starting $[Pt_2(pop)_4X_2]^{4-}$ species $[(d_\sigma)^2]$. In fact, the $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ complex, having the highest ϕ_r value[29] (Table II), has a Pt-Pt bond distance (2.782 (1) Å) close to that found in the partially oxidized linear-chain $[[Pt_2(pop)_4Br]^{4-}]$ compound (2.793 (1) Å).[25]

Conclusion

The efficient and stoichiometric photoconversion of $[Pt_2(pop)_4X_2]^{4-}$ to $[Pt_2(pop)_4]^{4-}$ in methanol makes $[Pt_2(pop)_4]^{4-}$ distinctly different from other binuclear d^8-d^8 complexes such as $[Rh_2(TMB)_4]^{2+}$ (TMB = 2,4-dimethyl-2,5-diisocyanohexane).[3] The high ϕ_r value observed for $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ suggests the potential usefulness of $[Pt_2(pop)_4]^{4-}$ in catalyzing photochemical C-X (X = halogen) bond-breakage reactions. Even though $[Pt_2(pop)_4]^{4-}$ is stable in aqueous solution, the complex nature of the photochemistry of $[Pt_2(pop)_4X_2]^{4-}$ in water precludes it to be a good solvent system for photocatalysis work.

Acknowledgment. Research at Hong Kong University (C.-M.C., W.-M.L.) was supported by the Committee of Conference and Research Grants of the University of Hong Kong. W.-M.L. acknowledges the receipt of a studentship, administered by the Croucher Foundation.

Registry No. $[Pt_2(pop)_4Br_2]^{4-}$, 87374-25-2; $[Pt_2(pop)_4Cl_2]^{4-}$, 87355-26-8; $[Pt_2(pop)_4Im_2]^{4-}$, 114944-21-7; $[Pt_2(pop)_4I_2]^{4-}$, 87355-25-7; $[Pt_2(pop)_4(SCN)_2]^{4-}$, 102133-43-7; $[Pt_2(pop)_4(CH_3)(I)]^{4-}$, 114928-99-3; $[Pt_2(pop)_4]^{4-}$, 80011-25-2.

Supplementary Material Available: Figures S1-S3 show spectral changes of photoreactions (3 pages). Ordering information is given on any current masthead page.

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(29) The high ϕ_r value for $[Pt_2(pop)_4(CH_3)(I)]^{4-}$ may also due to the fact that the reductively eliminated product, CH_3I, is nonoxidizing.

Aprotic Conjugate Addition of Allyllithium Reagents Bearing Polar Groups to Cyclic Enones. 1. 3-Alkylallyl Systems

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Abstract: The conjugate addition of lithiated (*E*)- and (*Z*)-oct-2-enyl sulfoxides and phosphine oxides, but-2-enyl sulfoxides, phosphine oxides and phosphonates, and 3,3-dimethylallyl and allyl sulfoxides to cyclic enones has been examined. The *E* and *Z* carbanions react in highly diastereoselective fashion with five-membered cyclic enones to deliver respectively syn and anti vinylic sulfoxides, phosphine oxides, and phosphonates. Hexamethylphosphoric triamide has no regiochemical influence on these reactions. The regiochemical and stereochemical outcomes of these reactions are rationalized in terms of planar lithiated reagents in which Li^+ is bound to oxygen attached to sulfur or phosphorus of the polar group and a 10-membered "trans-decalyl"- or "trans-fused chair-chair"-like transition-state model in which the lithiated reagent adopts an endo orientation over one face of the enone such that for the *E* reagent, the 3-alkyl group is pseudoequatorial, and for the *Z*, pseudoaxial.

The aprotic conjugate addition of lithiated stabilized carbanions to conjugated enones is a well-known reaction that has received considerable attention, from both exploratory mechanistic[1-4] and synthetic[5] viewpoints. In many cases, the propensity of such carbanions to undergo carbonyl addition with conjugated enones

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can be suppressed by conducting the reaction in the presence of hexamethylphosphoric triamide (HMPA).[2] In those cases where the carbanion is prochiral, or chiral, diastereomeric mixtures of conjugate addition products are generally obtained from prochiral enones without significant diastereoselection. Indeed, it is only in specialized cases involving enolates and acyclic enones that appreciable diastereoselection takes place.[3,4]

The reaction of stabilized *allylic* carbanions with conjugated enones is complicated by the ambident reactivity of the carbanion. Nevertheless, although lithiated allylic phenyl sulfides react by carbonyl addition with cyclopentenones to deliver regioisomeric mixtures of vinylic and allylic sulfides,[6,9] the presence of HMPA induces a kinetically controlled conjugate addition to take place with predominant or exclusive formation of allylic sulfides arising from reaction through C1 (Cα) of the carbanion.[6-8] Thus, from (*E*)-octenyl phenyl sulfide (**1**) (Chart I) and 4-*tert*-butoxycyclopent-2-enone (**17**) is obtained the allylic sulfide **2** as a 1:1 mixture of diastereomers in good yield.[7] The regiochemistry has been exploited in highly convergent syntheses of prostaglandin precursors.[9] During attempts to shorten the synthesis through use of lithiated allylic sulfoxides, we discovered that these reagents do not react in the same way as lithiated allylic sulfides with cyclopentenones.[10] Thus, lithiated allyl phenyl sulfoxide undergoes kinetically controlled conjugate addition to cyclopent-2-enone to give the vinylic sulfoxide **3** arising from reaction through C3 (Cγ) of the carbanion. This reaction, also independently reported by Pivnitskii and co-workers,[8] does not require HMPA. The anomaly becomes even more pronounced in light of the reactivity of lithiated allylic sulfones. Under the same conditions, these are reported to react in the same way as lithiated allylic sulfides in that HMPA causes kinetic conjugate addition to give allylic sulfones as mixtures of diastereomers.[11]

Intriguing as the regiochemical anomaly associated with the reactivity of the lithiated sulfoxides vis-à-vis the reactivities of the lithiated sulfides and sulfones is, of greater importance is the subsequent finding that the reactions involving lithiated allylic sulfoxides bearing alkyl groups at C3 (Cγ) and cyclopentenones are also highly diastereoselective; this adds enormously to the significance of these reactions. The diastereoselection is remarkable in view of the s-trans nature of the enone and because appreciable diastereoselection is not normally associated with aprotic conjugate addition reactions of this kind. In order to probe the causes of both the regiochemistry and the diastereoselectivity of these reactions, and to establish their scope and limitations, we examined the reactions of a number of lithiated allylic sulfoxides. During the course of the work, we also found that lithiated allylic phosphine oxides and phosphonates react in similar fashion. We now describe in detail the results of the study of these reactions, which as far as we are aware, have no close analogy in the literature.[12]

Chart I

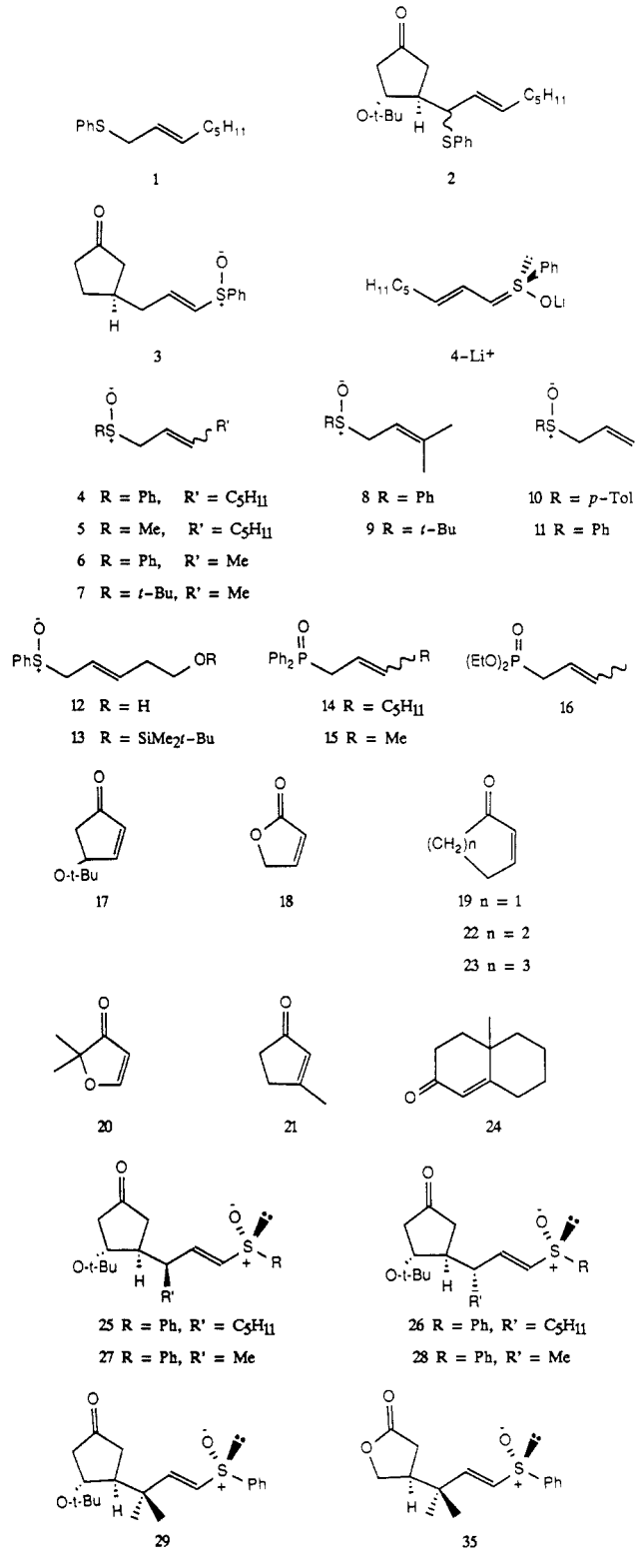

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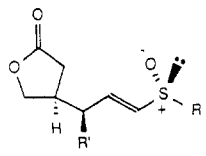
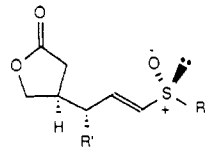
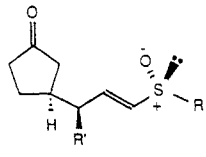
Chart II



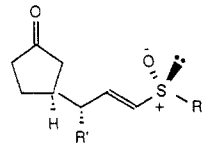
30 R = Ph, R' = C_5H_{11}
32 R = Me, R' = C_5H_{11}
33 R = Ph, R' = Me



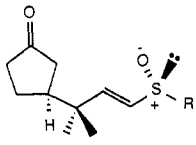
31 R = Ph, R' = C_5H_{11}
34 R = Ph, R' = Me



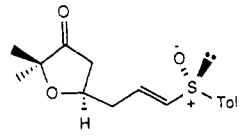
36 R = Ph, R' = Me
38 R = *t*-Bu, R' = Me
41 R = Ph, R' = CH_2CH_2OH
42 R = Ph, R' = $CH_2CH_2OSiMe_2t$-Bu



37 R = Ph, R' = Me



39 R = Ph
40 R = *t*-Bu



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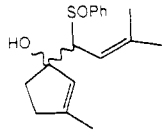

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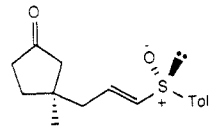

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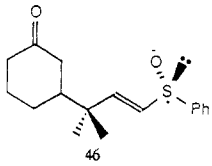

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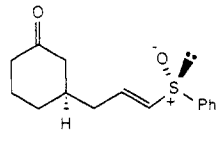

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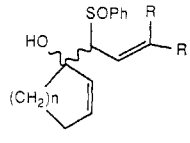
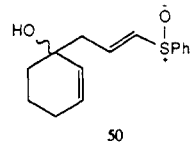


47 n = 2, R = Me
49 n = 2, R = H
51 n = 3, R = Me



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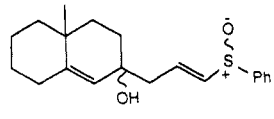

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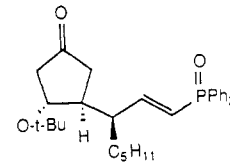
Chart III



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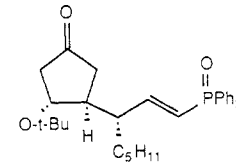

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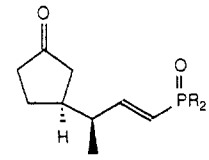
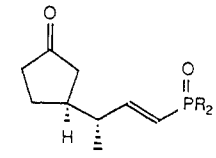


55 R = Ph
57 R = OEt



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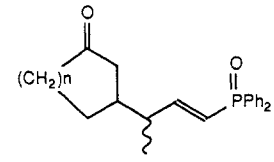
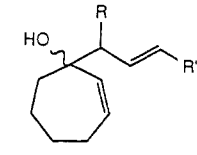
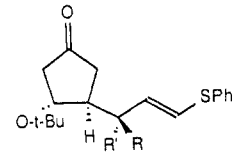


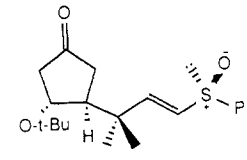
59 n = 2
60 n = 3



61 R = Me, R' = $POPh_2$
62 R = $POPh_2$, R' = Me



63 R = C_5H_{11}, R' = H
64 R = R' = Me



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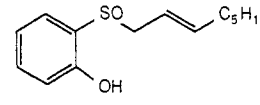

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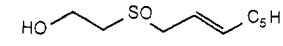

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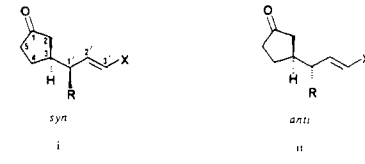
Results and Discussion

Addition of the enones **17–24** to the lithiated reagents derived from the allylic sulfoxides **4–13**, phosphine oxides **14** and **15**, and phosphonates **16** in THF and quenching the reaction mixture shortly thereafter gave the products **25–62** (Charts II and III). Overall yields and ratios of the products and geometric purity of the starting allylic sulfoxide, phosphine oxide, or phosphonate are summarized in Table I. Ratios of diastereomeric products were provided by 400-MHz ^1H NMR spectroscopic analyses of product mixtures. That the diastereochemical purity of the individual products could be assayed by NMR spectroscopy was checked by reducing the sulfoxides **25** and **29** with tributylphosphine–iodine in diethyl ether in the presence of HMPA[13] to the corresponding vinylic sulfides **63** and **64** and then reoxidizing these to sulfoxides with *m*-chloroperbenzoic acid. In both cases, the formation of diastereomeric sulfoxides was clearly indicated by the NMR spectra of the crude products; the diastereomeric sulfoxides **29** and **65** were also separated and characterized. We have described in detail elsewhere how the relative stereochemistries of the syn and anti[14] products **25** and **26** from the sulfoxide **4** and the enone

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

(14) The nomenclature of Masamune is used here to designate the relative disposition of substituents about the *newly created* adjacent chiral centers at C1′ and C3.[15] The syn diastereomer (for example, compound **25**) is taken to be that where C2 and the alkyl group (R) can be visualized as projecting toward the viewer, as in i. In the anti diastereomer (for example, compound



syn i anti ii

26), the alkyl group projects away, as in ii. C2 is chosen as one reference as it was originally within the enone system of the cyclopentenone. This has as analogy the use of the newly formed hydroxyl group in an aldol reaction as a reference in the syn–anti description of the stereostructures of the products.[15] The usage here is somewhat different from that usually employed for a description of the stereostructures of Michael adducts,[4] as in our case the "longest chain" commences at C1 and passes through C5, C4, and C3 of the cyclopentanone, and thence through C1′, C2′, and C3′ of the side chain.

Table I. Yields of Conjugate and Carbonyl Addition Products from Lithiated Sulfoxides, Phosphine Oxides, and Phosphonates

entry	enone	lithiated reagent	*E*:*Z* ratio	products		product ratio	overall yield,[a] %
				Sulfoxides			
1	**17**	**4**	90:10	**25**	**26**	90:10	79
2		**4**	17:83	**25**	**26**	21:79	70
3		**6**	80:20	**27**	**28**	80:20	64
4		**8**		**29**			80
5	**18**	**4**	85:15	**30**	**31**	83:17	83
6		**4**	17:83	**30**	**31**	20:80	80
7		**5**	92:8	**32**	*b*	92:8[b]	63
8		**6**	76:24	**33**	**34**	75:25	71
9		**8**		**35**			82
10	**19**	**6**	80:20	**36**	**37**	80:20	72
11							79 (−10 °C)
12		**7**	94:6	**38**	*b*	93:7[b]	71 (−10 °C)
13							80 (LiBr, −10 °C)[c]
14		**8**		**39**	*d*	80:20[d]	85
15							72 (Et_2O, −40 °C)[e]
16		**9**		**40**			57
17							80 (−20 °C)
18		**12**	85:15	**41**	*b*	85:15[b]	90
19		**13**	85:15	**42**	*b*	85:15[b]	73
20	**20**	**10**		**43**	*d*	83:17[d]	71
21	**21**	**8**		**44**	*g*		83
22		**10**		**45**			71
23							59 (HMPA)[f]
24	**22**	**8**		**46**	**47**[h]	58:42	79
25						65:35	85 (LiBr)[c]
26						60:40	77 (HMPA)[f]
27		**11**		**48**[i]		62:38[j]	59
				49[h]			10
				50[i]		55:45[j]	20
28	**23**	**8**		**51**[h]			77
29	**24**	**11**		**52**[g]			53
				Phosphine Oxides, Phosphonates			
30	**17**	**14**	95:5	**53**	**54**	95:5	81
31		**14**	17:83	**53**	**54**	18:82	83
32	**19**	**15**	>95.5:0.5	**55**			80
33		**15**	5:95	**55**	**56**	5:95	81
34		**16**	78:22	**57**	**58**	77:23	81
35		**16**	13:87	**57**	**58**	13:87	74
36	**22**	**15**	>95.5:0.5	**59**			73
37							85 (LiBr)
38	**23**	**15**	>95.5:0.5	**60**[i]		1:1[j]	27
				61[i]		60:40[j]	18.5
				62[i]		80:20[j]	42

[a] At −70 °C except where indicated. Yields refer to isolated, chromatographically pure products and are not adjusted to take account of small amounts of unchanged reactants also isolated. [b] Minor product not characterized; assumed to be anti compound. [c] Solution of enone containing LiBr (1–2 equiv) in THF added to lithiated reagent. [d] Minor product not characterized; assumed to differ in relative configuration at C3. [e] In diethyl ether as solvent. [f] Lithiated reagent generated in presence of HMPA (1–2 equiv). [g] Other, unstable products also formed. [h] Mixture of four diastereomers. [i] Mixture of two diastereomers. [j] Diastereomer ratios.

17 have been established through use of high-field ^1H NMR spectroscopy and an X-ray crystallographic study of a crystalline adduct formally derived from the syn product **25**.[16] The relative configuration at sulfur is provided by the X-ray study. Although the relative configuration at sulfur in the products from the (*Z*)-allylic sulfoxides was not determined, this must be the same as that in the products from the (*E*)-allylic sulfoxides, as is discussed below. X-ray data obtained from the product of another, more highly substituted (*Z*)-allylic sulfoxide described in the following paper confirm this.

From Table I, it is evident that the relative configuration at the allylic carbon atom in the products is dependent upon the geometry of the starting allylic compound: that is, (*E*)-allylic systems deliver syn products, and (*Z*)-allylic systems deliver anti products. When the allyl system bears an alkyl group at C3, then diastereoselection, within the limits of experimental error,[17] is virtually complete. Diastereoselection is poorest in the case of the allyl and dimethylallyl systems (entries 14, 20), except when the enone bears a methyl group at C3 (entry 22) or an alkoxy group at C4 (entry 4), or if the sulfoxide bears a bulky nonallylic group (entry 16). The reaction is also tolerant of moderate functionality in the lithiated sulfoxide (entries 18, 19). That products **41** and **42** obtained from these sulfoxides possess the same relative stereochemistry was shown by converting the latter into **41** by means of fluoride ion. Thus, the presence of a free hydroxyl group in the allylic sulfoxide, providing that it is distant from the allylic system, does not affect the stereochemical outcome of the reaction. If, however, there is a hydroxyl in the nonallylic group attached to sulfur as in compounds **66** and **67**, then regio- and stereoselection is destroyed.[12,18] When reaction through C3 of

(15) Masamune, S.; Ali, S. A.; Snitman, D. L.; Garvey, D. S. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 557. Heathcock, C. H. In Asymmetric Synthesis; Morrison, J. D., Ed.; Academic: Orlando, FL, 1984; Vol. 3, Part B, p 113.

(16) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Engelhardt, L. M.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 291. A summary of the NMR method and the preferred conformers of products **25**, **26**, **30**, and **31** as derived from the NMR data are given in the supplementary material.

(17) (*Z*)-Allylic phenyl sulfoxides readily isomerize at room temperature via the sulfoxide–sulfenate rearrangement to the *E* isomer. Consequently, it was not possible to measure with any degree of precision the composition of sulfoxide mixtures initially containing predominant amounts of the sulfoxide **6**.

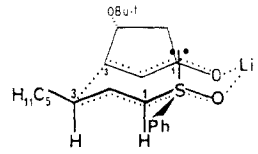


Figure 1. Trans-decalyl- or trans-fused chair–chair-like representation of the transition state of the reaction of lithiated (*E*)-octenyl sulfoxide **4** with 4-*tert*-butoxycyclopent-2-enone (**17**).

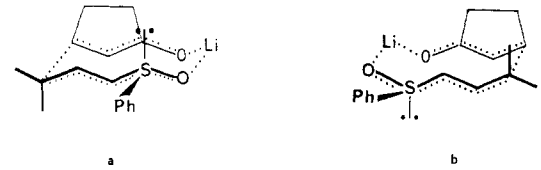


Figure 2. Trans-decalyl- or trans-fused chair–chair-like (a) and cis-fused boat–boat-like (b) representations of transition states of the reaction of lithiated (S_S)-sulfoxide **8** with cyclopentenone (**19**).

the enone is prevented, then carbonyl addition intervenes (entries 21, 29). This also takes place as the ring size of the enone increases (entries 24, 27–29, 38). The presence of HMPA has a somewhat deleterious effect upon yields (entry 23); in such cases increased amounts of starting materials are also isolated from the reaction mixture. The reagent does not suppress the formation of carbonyl addition products (entry 26). On the other hand, addition of enone in THF containing lithium bromide to the lithiated sulfoxide or phosphine oxide increases the yields of the conjugate addition products (entries 13, 25, 37). Reactions may be run at higher temperatures and also succeed in diethyl ether as solvent (entry 15).

In developing a model that is to account for these features, we consider first the structures of the lithiated carbanions, definitive data on which have not been recorded. ^{13}C NMR and ^1H NMR data of lithiated benzylic sulfoxides[19] and phosphonates[20] have been interpreted in terms of a planar carbanion, which in the case of the sulfoxide is ion-paired with the lithium counterion, presumably through the oxygen atom. It is significant that HMPA is unable to disrupt this ion pairing.[21] On the other hand, lithiated benzylic sulfides are pyramidal; disruption of the ion pair occurs in the presence of HMPA.[19] The hybridization state and general influence of coordinating solvents on ion pairing of sulfone carbanions appear to be intermediate between those of the sulfoxide and sulfide, although the effect of HMPA is similar to that which it exerts upon the ion-paired sulfide.[19] It is pertinent to note that X-ray crystal structure studies of lithiated alkyl phenyl sulfones indicate planar systems comparable to a lithium enolate in which one of the S–O bonds lies approximately in the nodal plane of the π-bond.[23] On the basis of this evidence and the following discussion, we represent the structure of the lithiated (*E*)-octenyl phenyl sulfoxide (**4**-Li$^+$) as an essentially *planar* system in which lithium is bound to oxygen and the C–S bond possesses double-bond character. C1–C2 has single bond, and C2–C3, double-bond character. The S–O and C1–C2 bonds are approximately antiperiplanar; that is, the former lies approximately in the nodal plane of the π-bond, a situation corresponding in part to that in lithiated benzylic sulfones.[23,24] There is thus a pyramidal arrangement of substituents about the sulfur atom, and so asymmetry is not lost through planarity at C1.

The formation of the product **25** can be accounted for by assuming that in the transition state the planar lithiated sulfoxide lies over one face of the enone such that it adopts an endo orientation with respect to the enone. Chelation of the lithium by the carbonyl oxygen may then be seen to serve as the regiochemical "anchor" which causes the sulfoxide group to lie over the carbonyl group. The carbanion is constrained to react through C3. The transition state itself is described as "trans-decalyl"-like or "trans-fused chair–chair"-like, as represented in Figure 1. The sulfoxide lone pair is pseudoaxial, and the phenyl is pseudoequatorial and projects away from the enone. The pentyl group as a consequence of the double-bond character of the C2–C3 bond in the lithiated sulfoxide must be pseudoequatorial in the TS. Although planar, the lithiated sulfoxide is possessed of diastereotopic faces, and it is because of both the configuration at sulfur and the endo orientation in the TS that reaction can only occur through the one face, as depicted. The chelation also accounts for the regiochemical differences in the reactivities of the lithiated sulfoxides vis-à-vis the sulfides as has also been noted by Pivnitskii and co-workers.[8] It also accounts for the anomalous reactivity of the lithiated reagents derived from the sulfoxides **68** and **69**, where internal coordination of lithium with alkoxide is likely. As a combination of orbital and charge control appears to be important in determining whether carbanions will undergo conjugate addition reactions to enones,[25] it is clear that the planar nature of the carbanion and its endo orientation with respect to the enone allow maximum orbital overlap between the reactants to operate. The HOMO of the lithiated sulfoxide, which can be considered as a heteropentadienyl system (cf. **4**-Li$^+$), interacts with the LUMO of the enone through the AOs at C1 and C3. Although this shall be discussed in more detail elsewhere in conjunction with MO calculations on the lithiated sulfoxides, we point out that orbital interactions between C1 of the reactants will confer the "decalyl"-like character of the TS.

The model adequately accounts for the features of the reactions as outlined above. Diastereoselection arises as a consequence of π-face selection by the lithiated sulfoxide. Where the enone is enantiofacial, as in enones **18–21**, the individual enantiomers of a lithiated racemic sulfoxide will react at opposite faces of the enone. When the enone bears a group that renders the faces diastereotopic, as in 4-*tert*-butoxycyclopent-2-enone (**17**), face selectivity is imposed by that group, and so individual enantiomers of the sulfoxide now undergo enantioselective reactions with the individual enantiomers of the enone. Given the face selectivity of the reaction, it is evident that the relative configuration at sulfur in the transition states involving the (*Z*)-sulfoxides must be the same as that in the (*E*)-sulfoxides. For the (*E*)-sulfoxide, the alkyl group at C3 is pseudoequatorial, whereas for the (*Z*)-sulfoxide, this is pseudoaxial. The increase in the amount of carbonyl addition associated with increasing ring size of the enone is attributed to enhanced diaxial interactions between H2 of the allyl system and the methylene protons at C5 or C6 of the enone destabilizing this transition state.[26] The presence of substituents that impose steric restraints to bond formation through C3 in either reactant will encourage the reaction to take place through C1 of the enone. Although within the context of the model (cf. Figure 1) there appears to be regiochemical significance in the formation of *allylic* sulfoxides arising from carbonyl addition (entries 24–27),

(18) Haynes, R. K.; Katsifis, A. G.; Chai, O. L., unpublished results.
(19) Chaissaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399.
(20) Bottin-Strzalko, T.; Seyden-Penne, J. *J. Org. Chem.* **1978**, *43*, 4346.
(21) The P–O dipole of phosphine oxides is generally greater than that of the S–O dipole of sulfoxides, thus making phosphine oxides the more effective lithium-complexing agent. However, the magnitude of the S–O dipole can be increased considerably when electron-donating substituents are adjacent to the S–O group.[22] Hence, the presence of an adjacent *carbanionic* site is expected to increase the magnitude of the dipole and, therefore, the complexing ability of the S–O group far beyond that observed in *neutral* sulfoxides and phosphine oxides. Thus, HMPA will have little effect on the ion pairs of a sulfoxide carbanion.
(22) Gurka, D.; Taft, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 4794. Szmant, H. H. In *Sulfur in Organic and Inorganic Chemistry*; Senning, A., Ed.; Marcell Dekker: New York, 1971; Vol. 1 p 142.
(23) Gais, H.-J.; Lindner, H. J.; Vollhardt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 859. See also: Boche, G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 573.
(24) The structures of lithiated sulfides are quite different. Lithiated (*E*)-but-2-enyl *tert*-butyl sulfide is shown through X-ray and computational studies to have lithium η^3 bound to the allyl system: Seebach, D.; Maetzke, T.; Haynes, R. K., Paddon Row, M. N.; Wong, S. S. *Helv. Chim. Acta* **1988**, *71*, 299.
(25) Deschamps, B.; Lefour, J.-M.; Loupy, A.; Seyden-Penne, J. *Nouv. J. Chim.* **1980**, *4*, 121, and references cited therein.
(26) Alternatively, this may reflect an attenuation in reactivity at C3 of larger ring enones arising through decreased orbital overlap between the carbonyl and conjugated alkene.

the lack of diastereoselection[27] implies that it does not necessarily proceed through extended transition states related to that of Figure 1; it must also involve the conventional size-membered transition states characteristic of the reaction of allylic nucleophiles with carbonyl compounds.[28] In this regard, the presence of two methyl groups at C3 of the allyl system, as in **8**, does not suppress the formation of a vinylic sulfoxide, in this case **46**, arising by conjugate addition to cyclohexenone, although only an allylic sulfoxide (**47**) is obtained from carbonyl addition. In the absence of the methyl groups, as in **11**, a vinylic sulfoxide (**50**) in addition to an allylic sulfoxide (**49**) is obtained from carbonyl addition (entries 24, 27). As HMPA will not solvate Li^+ when this is associated with negatively charged sulfoxide,[21] regiochemistry is unaffected by the reagent. The lower yields of products obtained in its presence are associated with an increase in recovery of unreacted starting material; proton transfer from the enone to the lithiated sulfoxide is presumably enhanced by the presence of HMPA. The role of lithium bromide in enhancing the yields of the conjugate addition products may be associated with suppression of proton transfer.[29]

The lower stereoselectivity associated with the reactions of the allyl and dimethylallyl sulfoxides (entries 14, 20, Table I) is intriguing and is best understood by considering the reactions of a single enantiomer of the starting racemic sulfoxide. The (S_s) enantiomer of the sulfoxide **8** will deliver the ($3S,S_S$) enantiomer of the major product **39** through the normal TS involving the *si* face of the enone (Figure 2). The minor product obtained from the (S_S)-sulfoxide clearly must possess the same configuration at sulfur; it thus can *only* differ in configuration at C3 within the cyclopentanone nucleus. It must as a consequence arise through reaction at the *re* face of the starting enone. The one extended transition state—described as "cis-fused boat–boat"-like—that can be drawn to accommodate these stereochemical requirements is given in Figure 2. Although obviously disfavored with respect to the first TS of Figure 2,[30] further examples of reactions proceeding through this TS are known and are given in the accompanying paper. It now becomes clear that this "unwanted" reaction pathway involving the allyl and dimethylallyl sulfoxides can be blocked through the attachment of groups at either C3 (entry 22) or C4 of the enone (entry 4)[31] or through use of a larger nonallylic substituent—*tert*-butyl—attached to sulfur (entry 16).

The model of the TS as encapsulated in Figure 1 clearly indicates that lithiated carbanions which have allylic geometry and polar groups sterically and electronically related to sulfoxide should also undergo conjugate addition. It was on this basis that an examination of the reactions of lithiated allylic phosphine oxides and phosphonates was undertaken. The carbanions must be structurally similar to the sulfoxides and are assumed to be planar; the oxygen atom is predicted to lie approximately within the nodal plane of the π-bond, and the spatial arrangement of the two nonallylic substituents is as for the lone-pair and nonallylic substituent in the lithiated sulfoxide. An obvious analogy may be drawn with the structure of the sulfone discussed above.[23] The presence of two nonallylic substituents attached to phosphorus renders the carbanions somewhat more hindered than the sulfoxides, and it may be for this reason that carbonyl addition through C1 is less favored than in the case of the sulfoxide (entries 24–28, 36, 37).

Regardless of the actual mechanism by which these reactions proceed, the model of the mechanism we have presented is conceptually simple, easily visualized, and consistently accounts for the regiochemical and stereochemical features of the reactions. Although the regiospecific formation of the vinylic products is synthetically useful,[32] the great value of the reactions obviously lies in the virtually quantitative translation of the *E* or *Z* geometry of the starting allylic system into syn or anti compounds that possess a level of functionality suitable for abundant synthetic exploitation. The reactions also appear to be unique in that face selectivity is brought about through a structural feature inherent in the carbanion, and so they do not rely on the usual devices required to bring about face selection in conjugate addition—an exogenous group shielding one face of the enone, or a discrete chiral complexing agent associated with the carbanion. Further, the conjugate addition produces a lithium enolate whose reaction with a suitable electrophile enables further functionality to be added in a stereocontrolled fashion.[33]

Finally, it needs to be pointed out that if these reactions are to be successfully applied to enantiomerically pure phosphine oxides and phosphonates, then these reagents have to bear nonallylic substituents attached to phosphorus that have substantially different steric requirements. There has to be a clear preference for one substituent to adopt a pseudoequatorial, the other a pseudoaxial, disposition in the TS, otherwise face selectivity will be lost and mixtures of diastereomers will result.[34] In this regard, the optimum substrates are obviously sulfoxides, but unfortunately the difficulties associated with the preparation and stability of optically active 3-alkylallylic sulfoxides preclude their general use in this regard. However, optically active allyl bornyl sulfoxides derived from camphor[35] and (+)-(*R*)-allyl tolyl sulfoxide[36] have been successfully used. In the latter case, the structures of the products have been established by correlation with a cyclopentanone of known absolute configuration. The stereochemical outcome of these reactions are as predicted by the model.

Experimental Section

General Aspects. The general experimental conditions have been described previously.[7] Cyclopent-2-enone,[37] 4-*tert*-butoxycyclopent-2-enone,[38] but-2-en-4-olide (γ-crotonolactone),[39] 2,2-dimethyl-3(2*H*)-furanone,[40] and 4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalene[41]

(27) As is clearly apparent from 400-MHz spectra recorded on crude reaction mixtures directly after workup, allylic sulfoxides arising from carbonyl addition are obtained as mixtures of four diastereomers. In all cases, the ratio of diastereomers changes with time, presumably through equilibration via the sulfoxide–sulfenate rearrangement.

(28) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555. Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: Orlando, FL, 1984; Vol. 3, Part B, pp 154–159, and references cited therein.

(29) Ahlbrecht, H.; Kompter, H.-M. *Synthesis* **1983**, 645. We initially anticipated that complexation of the enone by "external" Li^+ would encourage carbonyl addition by disrupting chelation and enhancing the charge-control effects considered to be important in carbonyl addition.[25] It seems that complexation enhances the electrophilic nature of the enone so that proton transfer is suppressed in favor of conjugate addition. Presumably, "displacement" of enone-complexed Li^+ by sulfoxide-bound Li^+ occurs in the TS.

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

(31) In 4-*tert*-butoxycyclopent-2-enone, the *tert*-butoxy group ensures that H4 is approximately pseudoaxial.[7,16] There will thus be a more rigid and crowded environment about C4 than in cyclopent-2-enone; this will destabilize a "cis-fused boat–boat"-like TS of Figure 2 in favor of the normal "trans-fused chair–chair"-like TS in reactions involving this enone.

(32) The regiochemical aspect of these reactions has been exploited in the case of vinylic sulfoxides obtained from allylic sulfoxides bearing an alkyl group at C1: Vasil'eva, L. L.; Mel'nikova, V. I.; Pivnitskii, K. K. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 2346. Nokami, T.; Ono, A.; Iwao, A.; Wakabayshi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3043. Vasil'eva, L. L.; Mel'nikova, V. I.; Pivnitski,, K. K. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 628. Nokami, J.; Ono, T.; Wakabayashi, S.; Hazato, A.; Kurozumi, S. *Tetrahedron Lett.* **1985**, *26*, 1985.

(33) Haynes, R. K.; Vonwiller, S. C. *J. Chem. Soc., Chem. Commun.* **1987**, 92. Haynes, R. K.; Katsifis, A. G. *J. Chem. Soc., Chem. Commun.* **1987**, 340.

(34) This is verified in the very recent work of Hua and co-workers involving conjugate additions with lithiated chiral allyl oxazaphospholidine oxides: Hua, D. H.; Chan-Yu-King, R.; McKie, J. A.; Myer, L. *J. Am. Chem. Soc.* **1987**, *109*, 5026.

(35) Binns, M. R.; Goodridge, R. J.; Haynes, R. K.; Ridley, D. D. *Tetrahedron Lett.* **1985**, *26*, 6381.

(36) Hua, D. H.; Sinai-Zingde, G.; Venkataraman, S. *J. Am. Chem. Soc.* **1985**, *107*, 4088. Hua, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 3835. Hua, D. H.; Venkataraman, S.; Coulter, M. J.; Sinai-Zingde, G. *J. Org. Chem.* **1987**, *52*, 719 The preparation of compounds **43** and **45** in enantiomerically enriched forms were reported by Hua and co-workers.

(37) Alder, K.; Flock, F. H. *Chem. Ber.* **1956**, *89*, 1732.

(38) Haubenstock, H.; Mennitt, P. G.; Butler, P. E. *J. Org. Chem.* **1970**, *35*, 3728. Schwartz, J. A.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980**, *102*, 3728.

(39) Price, C. C.; Judge, J. M., *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. 1, p 254. Takano, S.; Ogasawara, K. *Synthesis* **1974**, 42.

(40) Margaretha, P. *Tetrahedron Lett.* **1971**, 4891.

were prepared according to literature procedures. ^1H NMR spectra were recorded at 400 MHz, unless indicated otherwise.

Preparation of (1) Allylic Sulfoxides. These were prepared by oxidation of the corresponding sulfides with *m*-chloroperoxybenzoic acid (1.2 equiv) in dichloromethane at −70 °C followed by removal of the *m*-chlorobenzoic acid by filtration and evaporation of solvent from the filtrate under reduced pressure at 0 °C. The residue was taken into diethyl ether, and the ether solution was washed with aqueous potassium carbonate and brine, dried, and evaporated under reduced pressure at 0 °C. The residue was submitted to flash chromatography with ethyl acetate–light petroleum to give the sulfoxide as a colorless oil. *E*:*Z* ratios were established by ^1H and ^{13}C NMR spectroscopy, except where indicated.

1-(Phenylsulfinyl)oct-2-ene (4). 1-(Phenylthio)oct-2-ene (*E*/*Z* 90:10)[42] was converted into the sulfoxide **4** (*E*/*Z* 90:10).[43] Distillation of the product at 155–160 °C (0.2 mm) caused the amount of *Z* isomer to increase to 20%. 1-(Phenylthio)oct-2-ene (*Z*/*E* 88:12)[42] gave the sulfoxide **4** (*Z*/*E* 83:17), which was stored at −20 °C and used within 24 h of its preparation. After 48 h at room temperature, the mixture contained 50% of the (*E*) isomer: ^1H NMR (100 MHz) δ 0.7–1.0 (3 H, m, H8), 1.0–1.5 (6 H, m, H5, H6, H7), 1.6–2.2 (2 H, m, H4), 3.59 (2 H, d, *J* = 8 Hz, H1), 5.25 (1 H, dt, *J* = 10, 7.5 Hz, H3), 5.72 (1 H, dt, *J* = 10, 8 Hz, H2).

1-(Methylsulfinyl)oct-2-ene (5). (*E*)-1-(Methylthio)oct-2-ene[51] gave the sulfoxide **5** (*E*/*Z* 92:8): IR (neat) ν_{max} 3450 (br), 2940 (br), 1740 (m), 1660 (w), 1470 (m), 1380 (w), 1300 (m), 1290 (m), 1270 (m), 1330 (w), 1110 (w), 1060 (w), 980 (s), 840 (w), 760 (w), 740 (w) cm^{-1}; ^1H NMR (100 MHz) δ 0.77–1.00 (3 H, m, H8), 1.15–1.59 (6 H, m, H5, H6, H7), 1.97–2.25 (2 H, m, H4), 2.52 (3 H, s, $SOCH_3$), 3.41 (2 H, d, *J* = 7.0 Hz, H1), 5.49 (1 H, dtt, *J* = 15.0, 7.0, 1.2 Hz, H2), 5.84 (1 H, dt, *J* = 15.0, 6.6 Hz, H3); MS *m*/*e* 174 (M^+, <1), 139 (3), 81 (10), 70 (10), 69 (100), 67 (15), 64 (10), 63 (12), 57 (18), 55 (85), 53 (32); HRMS calcd for [$C_9H_{18}OS$ − O] 158.1078, found 158.1073.

1-(Phenylsulfinyl)but-2-ene (6). Freshly prepared, crude 1-bromobut-2-ene[44] [*E*/*Z* 95:5, according to GC analysis (10% Carbowax 20M on Gas Chrom Q, 1.46 m × 2 mm i.d. column, column temperature 62 °C, N_2 flow rate 25 mL min^{-1})] was converted by a standard method into 1-(phenylthio)but-2-ene (*E*/*Z* 95:5), bp 130 °C (0.7 mm; Kugelrohr) [lit.[45] bp 69.6–70.0 °C (1.3 mm)], and thence into the sulfoxide **6** [*E*/*Z* 82:18, according to HPLC (1:3 ethyl acetate–light petroleum, Brownlee column, SI 100, 5 μm, flow rate 1 mL/min)]. Distillation at 120–123 °C (0.5 mm; Kugelrohr) caused the *E*:*Z* ratio to change to 3:1. The spectroscopic properties of this compound were in agreement with those reported for a 3:1 mixture of the isomers.[46]

1-[(1,1-Dimethylethyl)sulfinyl]but-2-ene (7). Sodium 2-methylpropane-2-thiolate (91 mmol) in methanol (100 mL) at 0 °C was treated dropwise with (*E*)-1-bromobut-2-ene (12.96 g, 96 mmol). The resultant solution was stirred at 0 °C for 3 h and then poured into water and extracted with ether. The combined extracts were washed with aqueous potassium carbonate and brine and then dried (Na_2SO_4). Evaporation of the solvent left a pale yellow oil (12.74 g), which was distilled to yield the sulfide as a colorless liquid [*E*/*Z* 94:6, according to GC analysis (SGE fused silica Superox 0.1 50 m × 0.33 mm i.d. capillary column, column temperature 80 °C, He pressure 90 kPa): 11.44 g, 87%; bp 115 °C (18 mm; IR (neat) ν_{max} 2960 (br s), 2860 (sh), 1450 (m), 1410 (w), 1190 (m), 980 (m), 940 (w) cm^{-1}; ^1H NMR (90 MHz) δ 1.31 (9 H, s, *t*-Bu), 1.70 (3 H, dm, *J* = 4.9 Hz, H4), 3.16 (2 H, dm, *J* = 4.8 Hz, H1), 5.41–5.65 (2 H, m, H2, H3); MS *m*/*z* 144 (M^+, 21), 88 (24), 57 (100), 55 (59), 54 (22); HRMS calcd for $C_8H_{16}S$ 144.0973, found 144.0976. Anal. Calcd for $C_8H_{16}S$: C, 66.6; H, 11.2. Found: C, 66.3; H, 11.1. From the sulfide was obtained after flash chromatography with 20:80 ethyl acetate–light petroleum the sulfoxide **7** (*E*/*Z* 94:6): IR (neat) ν_{max} 2963 (s), 2920 (sh, s), 1474 (m), 1462 (m), 1439 (sh), 1365 (m), 1184 (m), 1038 (s), 968 (m) cm^{-1}; ^1H NMR (100 MHz) δ 1.26 (9 H, s, *t*-Bu), 1.71–1.82 (3 H, m, H4), 2.97–3.39 (2 H, m, H1), 5.59 (1 H, ddd, *J* = 15.3, 6.5, 5.7 Hz, H2), 5.83 (1 H, dq, *J* = 15.3, 5.7 Hz, H3); MS (CI) *m*/*e* 161 (M + 1, 23), 145 (3), 133 (9), 105 (34), 87 (32), 57 (53), 43 (58), 41 (73), 31 (61), 30 (25), 29 (100), 28 (62). Anal. Calcd for $C_8H_{16}OS$: C, 59.95; H, 10.1. Found: C, 59.6; H, 10.2.

3-Methyl-1-(phenylsulfinyl)but-2-ene (8). 1-(Phenylthio)-3-methylbut-2-ene[47] gave after flash chromatography with 40:60 ethyl acetate–light petroleum the sulfoxide **8** as a pale yellow oil: bp 172–175 °C (0.1 mm; Kugelrohr) IR (neat) ν_{max} 2970 (s), 2930 (s) 1580 (w), 1440 (s), 1380 (m), 1220 (w), 1080 (s), 1040 (br, s), 900 (m), 840 (s), 740 (s) cm^{-1}; ^1H NMR δ 1.36 (3, s, CH_3), 1.67 (3 H, s, CH_3), 3.55 (2 H, d, *J* = 8.1 Hz, CH_2), 5.07 (1 H, tm, *J* = 8.1 Hz, H2), 7.35–7.70 (5 H, m, C_6H_5); MS *m*/*e* 195 (7), 194 (M^+, 5), 126 (80), 125 (22), 110 (17), 109 (16), 97 (10), 78 (60), 77 (30), 69 (100); HRMS calcd for $C_{11}H_{14}O_2S$ 194.0765, found 194.0765.

1-[(1,1-Dimethylethyl)sulfinyl]-3-methylbut-2-ene (9). Treatment of sodium 2-methylpropane-2-thiolate (56 mmol) in methanol (60 mL) with 1-bromo-3-methylbut-2-ene (8.3 g, 56 mmol) gave the sulfide as a pale yellow oil (7.1 g, 81%): bp 36–37 °C (0.8 mm); IR (neat) ν_{max} 2900 (br s), 1450 (s), 1420 (m), 1190 (s), 860 (s) cm^{-1}; ^1H NMR (90 MHz) δ 1.31 (9 H, s, *t*-Bu), 1.66 (3 H, s, CH_3), 1.69 (3 H, s, CH_3), 3.16 (2 H, d, *J* = 7.8 Hz, CH_2), 5.22 (1 H, tqq, *J* = 7.8, 1.5, 1.5 Hz, H2); MS *m*/*e* 158 (M^+, 40), 102 (12), 91 (5), 69 (100), 57 (60), 41 (55). Anal. Calcd for $C_9H_{18}S$: C, 68.35; H, 11.4. Found: C, 68.0; H, 11.0. From the sulfide was obtained after flash chromatography with 30:70 ethyl acetate–light petroleum the sulfoxide **9**: bp 125–130 °C (0.5 mm; Kugelrohr); IR (neat) ν_{max} 2960 (br, s), 1640 (w), 1440 (s), 1410 (s), 1330 (m), 1130 (m), 1050 (s), 850 (w) cm^{-1}; ^1H NMR (90 MHz) δ 1.25 (9 H, s, *t*-Bu), 1.70 (3 H, s, CH_3), 1.78 (3 H, s, CH_3), 3.20 (2 H, d, $J_{1,2}$ = 7.8 Hz, CH_2), 5.30 (1 H, tqq, $J_{2,1}$ = 7.8, $J_{2,Me}$ = 1.5, Hz, H2); MS *m*/*e* 174 (M^+, 1), 158 (1), 156 (1), 139 (1), 118 (2), 106 (3), 91 (1), 69 (100), 57 (50), 41 (75). Anal. Calcd for $C_9H_{18}OS$: C, 62.1; H, 10.3. Found: C, 62.5, H, 10.0.

5-(Phenylsulfinyl)pent-3-en-1-ol (12). A solution of 3-(phenylthio)-pent-4-en-1-ol[48] (10 g, 52 mmol) in dichloromethane (150 mL) in a Pyrex flask was exposed to strong sunlight for 12 h. Evaporation of the dichloromethane followed by flash chromatography with 80:20 ethyl acetate–light petroleum gave the sulfide (9.3 g, 93%) as a colorless oil: IR (neat) ν_{max} 3350 (s), 2960 (s), 1590 (s), 1490 (s), 1490 (s), 1450 (s), 1230 (w), 1050 (s), 970 (s), 740 (s) cm^{-1}; ^1H NMR (100 MHz) δ 1.64 (1 H, s, OH), 2.10–2.35 (1 H, m, H1), 3.45–3.75 (4 H, m, H2, H5), 5.45–5.80 (2 H, m, H3. H4), 7.18–7.45 (5 H, m, C_6H_5); MS *m*/*e* 194 (M^+, 2), 156 (2), 110 (100), 109 (30). Anal. Calcd for $C_{11}H_{14}OS$: C, 68.0; H, 7.2. Found: C, 68.0; H, 7.3. This gave after flash chromatography with 60:40 ethyl acetate–light petroleum the sulfoxide **12** (*E*/*Z* 85:15): IR (neat) ν_{max} 3400 (br, s), 2940 (s), 1600 (w), 1480 (m), 1450 (m), 1310 (s), 1240 (m), 1150 (s), 1090 (m), 1050 (s), 1000 (m), 970 (m), 750 (s), 690 (s) cm^{-1}; ^1H NMR (90 MHz) δ 2.10–2.35 (2 H, m, H2), 3.30–3.75 (5 H, m, H2, H5, OH), 5.05–5.80 (2 H, m, H3, H4), 7.35–7.70 (5 H, m, C_6H_5); MS *m*/*e* 194 (M^+, 2), 156 (2), 126 (100), 125 (40), 110 (50), 109 (30). Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.9; H, 6.7. Found: C, 63.0; H, 7.2.

5-(Phenylsulfinyl)pent-3-enyl Dimethyl(1,1-dimethylethyl)silyl Ether (13). A solution of 5-(phenylthio)pent-3-en-1-ol (10 g, 51.5 mmol) in dichloromethane (120 mL) containing tetramethylethylenediamine 6.0 g, 51 mmol) was treated with *tert*-butyldimethylsilyl chloride (9.3 g, 61.8 mmol). The resultant mixture was stirred for 1.5 h, and the dichloromethane was thereupon evaporated. The residue was extracted with light petroleum (3 × 100 mL), and the extracts were washed successively with saturated citric acid (3 × 60 mL), aqueous potassium carbonate (10%, 40 mL), and brine. The solution was dried (Na_2SO_4) and the solvent evaporated under reduced pressure to leave a light yellow oil, distillation of which gave the silyl ether as a colorless liquid (12.1 g, 76%): bp 195–205 °C (0.4–0.5 mm); IR (neat) ν_{max} 2940 (s), 2850 (m), 1590 (m), 1480 (s), 1440 (m), 1390 (m), 1360 (m), 1260 (s), 1230 (m), 1090 (s), 1030 (m), 1010 (m), 970 (m), 940 (m), 840 (s), 780 (m), 740 (m), 690 (m) cm^{-1}; ^1H NMR (100 MHz) (CH_2Cl_2 reference) δ 0.09 (6 H, s, CH_3), 0.95 (9 H, s, *t*-Bu), 2.10–2.42 (2 H, m, H2), 3.45–3.80 (4 H, m, H1, H5), 5.50–5.70 (2 H, m, H3, H4), 7.20–7.45 (5 H, m, C_6H_5); MS (CI) 309 (P + 1). Anal. Calcd for $C_{17}H_{28}OSSi$: C, 66.2; H, 9.1; S, 9.9. Found: C, 66.5; H, 9.5; S, 10.2. The sulfide gave after flash chromatography with 10:90 ethyl acetate–light petroleum the sulfoxide (**13** (*E*/*Z* 85:15): IR (neat) ν_{max} 2970 (sh), 2950 (s), 2870 (sh), 1480 (m), 1460 (m), 1400 (w), 1270 (s), 1110 (s), 1060 (s), 980 (m), 850 (s), 790 (s), 760 (s) cm^{-1}; ^1H NMR (100 MHz) (CH_2Br_2 reference) δ 0.04 (6 H, s, CH_3), 0.90 (9 H, s, *t*-Bu), 2.1–2.4 (2 H, m, H2), 3.4–3.7 (4 H, m, H1, H5), 5.2–5.8 (2 H, m, H3, H4), 7.45–7.65 (5 H, m, C_6H_5); MS *m*/*e* 324

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(M^+, <1), 309 (M^+ - 16, <1), 267 (10), 240 (10), 227 (18), 213 (10), 183 (20), 167 (30). Anal. Calcd for $C_{17}H_{28}O_2SSi$: C, 63.0; H, 8.6; S, 9.9. Found: C, 63.0; H, 8.9; S, 10.2.

(2) Phosphine Oxides. Oct-2-enyldiphenylphosphine Oxide (14). Oct-1-en-3-ol (5.3 g, 41.5 mmol) in dry pyridine (80 mL) under nitrogen was treated dropwise with freshly distilled chlorodiphenylphosphine (10 g, 45.5 mmol) at room temperature. After ca. 15 min, the resulting mixture was heated to reflux for 3 h under nitrogen, cooled, and then poured into 1 M hydrochloric acid and extracted with diethyl ether (2 × 150 mL) and chloroform (200 mL). The combined extracts were washed repeatedly with 1 M and then 3 M HCl until the aqueous phase was acidic. Washing with brine, drying (Na_2SO_4), and evaporation of the solvent left a pale yellow oil. Purification by flash chromatography with 80:20 ethyl acetate–light petroleum gave the phosphine oxide as a colorless, viscous oil (E/Z 95:5) (10.8 g, 84%). Upon standing at 4 °C, the oil slowly solidified to a white waxy solid: mp 31–36 °C; IR (neat) ν_{max} 2930 (s), 1710 (w), 1600 (w), 1490 (w), 1470 (m) 1440 (s), 1410 (m), 1200 (s), 1130 (s), 1110 (m) cm^{-1}; ^1H NMR (400 MHz) δ 0.82 (3 H, t, J = 7.5 Hz, H8), 1.06–1.28 (6 H, m, H5, H6, H7), 1.88–2.97 (2 H, m, H4), 3.08 (2 H, dd, J = 14.3, 6.5 Hz, H1), 5.38–5.54 (2 H, m, H2, H3), 7.4–7.8 (10 H, m, C_6H_5); MS m/e 312 (M^+, 34), 203 (12), 202 (100), 201 (90), 183 (4), 125 (5). Anal. Calcd for $C_{20}H_{25}OP$: C, 76.9; H, 8.0. Found: C, 76.6; H, 7.9. 1-Bromooct-2-ene (Z/E 89:11)[42] (5.4 g, 28 mmol) was added slowly dropwise to a solution of lithium diphenylphosphide, prepared from diphenylphosphine (5.3 g, 28 mmol) and butyllithium (12.9 mL, 2.4 M, 31 mmol) in THF (150 mL) at −40 °C. The bright red of the phosphide anion changed to brown-black during the addition. The resulting solution was stirred for 30 min at 0 °C and was then quenched with aqueous ammonium chloride and extracted with chloroform (2 × 100 mL). The extracts were washed successively with aqueous hydrogen peroxide (5%, 125 mL), aqueous sodium sulfite (10%, 50 mL), aqueous sodium hydrogen carbonate (5%, 50 mL), and brine and then dried (Na_2SO_4). Evaporation of the solvent left a pale yellow oil, purification of which by flash chromatography with 80:20 ethyl acetate–light petroleum gave the phosphine oxide as a colorless viscous oil (Z/E 83:17) (6.2 g, 70%). Upon standing, the oil slowly solidified to an amorphous white solid, mp 56–57 °C, which could not be crystallized: IR (neat) ν_{max} 3150 (sh), 3040 (s), 1720 (w), 1600 (w), 1490 (m), 1470 (s), 1440 (s), 1420 (m), 1340 (w), 1320 (w), 1200 (s), 1130 (s), 1080 (m), 1040 (m), 1000 (m) cm^{-1}; ^1H NMR δ 1.83 (3 H, t, J = 7.5 Hz, CH_3), 1.07–1.36 (6 H, m, H5, H6, H7), 1.85–1.94 (2 H, m, H4), 3.15 (2 H, dd, J = 14.75, 7.5 Hz, H1), 5.41–5.46 (1 H, m, H2 or H3), 5.53–5.57 (1 H, m, H3 or H2), 7.40–7.80 (10 H, m, C_6H_5); MS m/e 312 (M^+, 15), 203 (20), 202 (100), 201 (70), 183 (3), 125 (6). Anal. Calcd for $C_{20}H_{25}OP$: C, 76.9; H, 8.0. Found: C, 76.6; H, 7.9.

But-2-enyldiphenylphosphine Oxide (15). From chlorodiphenylphosphine (22.55 g, 0.102 mol, 18.3 mL) and but-3-en-2-ol (7.34 g, 85 mmol) in dry pyridine (120 mL) according to the above was obtained the crude phosphine oxide (E/Z 91:9). Flash chromatography with 80:20 ethyl acetate–light petroleum and recrystallization from ethyl acetate gave the E isomer of **15** as fine needles (14.42 g, 66%), mp 118–120 °C (lit.[49] mp 118–119 °C). Analysis by ^1H NMR spectroscopy (400 MHz) showed the phosphine oxide to contain <0.5% of the Z isomer. Crude (Z)-1-bromobut-2-ene[50] (2.9 g, 21 mmol) was added slowly to lithium diphenylphosphide, prepared from diphenylphosphine (4.0 g, 21.5 mmol) and butyllithium (9.8 mL, 2.4 M, 23 mmol) in THF (80 mL) at −40 °C under nitrogen. Workup according to conditions described above gave a yellow solid, purification of which by flash chromatography with 50:50 ethyl acetate–light petroleum ether and recrystallization from ethyl acetate–hexane gave the phosphine oxide **15** (Z/E 95:5) (3.8 g, 70%) as fine white prisms, mp 111–112 °C (lit.[49] mp 111–112.5 °C).

(3) Phosphonates. Diethyl But-2-enylphosphonate (16). Triethyl phosphite (10.5 g 63 mmol) and commercial 1-bromobut-2-ene (E/Z 4:1) (8.5 g 63 mmol) under reflux during 3 h gave the phosphonate **16** (E/Z 80:20) [bp 90–95 °C (0.5 mm; Kugelrohr) [lit.[51] bp 110.5 °C (7 mm)]]. A stirred solution of diethyl phosphite (4.5 g, 32.6 mmol) in THF (100 mL) at −10 °C under nitrogen was treated first with butyllithium (14.5 mL, 2.3 M, 32.6 mmol) and then after 5 min with a solution of (Z)-1-bromobut-2-ene (4.0 g, 29.6 mmol) in THF (10 mL). The resulting solution was stirred for a further 10–15 min with warming to 0 °C and then quenched with aqueous ammonium chloride. The reaction mixture was extracted with ether, and the extracts were washed with brine and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure left a pale yellow oil, which was distilled to give the phosphonate (Z/E 87:13) as a colorless liquid (4.9 g, 86%): bp 130–140 °C (0.5 mm); IR (neat) ν_{max} 2990 (s), 2940 (br, s), 1660 (w), 1450 (m), 1390 (m), 1370 (w), 1250 (s), 1170 (m), 1060 (s), 1030 (s), 970 (s), 850 (m) cm^{-1}; ^1H NMR δ 1.321 (6 H, td, J = 7.2, 0.45 Hz, CH_3), 1.67 (3 H, dddd, J = 6.5, 3.5, 0.8, 0.8 Hz, H4), 2.62 (2 H, dddd, J = 20.1, 7.0, 0.9, 0.8 Hz, H1), 4.11 (4 H, dq, J = 10, 7.0 Hz, CH_2), 5.45 (1 H, dddm, J = 14.9, 10, 6.5, 0.9 Hz, H2), 5.70 (1 H, dddq, J = 19.2, 10, 7.0, 3.6 Hz, H3); MS m/e 193 (18), 192 (M^+, 60), 177 (31), 164 (20), 149 (16), 138 (60), 137 (15), 136 (77), 135 (15), 125 (16), 124 (20), 121 (20), 111 (75), 82 (82), 55 (100); HRMS calcd for $C_8H_{17}O_3P$ 192.0915, found 192.0910.

Conjugate Addition of (1) Lithiated Allylic Sulfoxides. General Method. The sulfoxide (1–3 mmol) in THF (1–3 mL) was added slowly dropwise to a slight excess of lithium diisopropylamide (1.1 equiv), generated from butyllithium and diisopropylamine in the presence of 2,2′-bipyridyl as indicator in THF (20–35 mL) at −70 °C under nitrogen. The solution was stirred for 5 min, and the carbanion was treated at −70 °C, except where indicated, with an equivalent quantity of the enone dissolved in THF (2–4 mL). Addition of the enone was carried out slowly so as to ensure that the reaction temperature remained constant. The mixture was then quenched with aqueous ammonium chloride and extracted with diethyl ether. The ether extract was washed with brine, dried, and evaporated to leave the crude product, which was assayed by 400-MHz NMR prior to and after purification by flash chromatography and/or HPLC.

4-*tert*-Butoxycyclopent-2-enone with (i) 1-(Phenylsulfinyl)oct-2-ene (4). From the sulfoxide (E/Z 90:10) (411 mg, 1.73 mmol) and the enone (301 mg, 1.95 mmol) was obtained after flash chromatography with 40:60 ethyl acetate–light petroleum a 90:10 mixture of the (1′*RS*,2′*E*,3*SR*,4*RS*,R_SS_S) and (1′*RS*,2′*E*,3*RS*,4*SR*,S_SR_S) diastereomers **25** and **26** of *3-(1,1-dimethylethoxy)-4-[1′-pentyl-3′-(phenylsulfinyl)-prop-2′-enyl]cyclopentanone* (531 mg, 79%) as a colorless oil. The major isomer was isolated by analytical HPLC (40:60 ethyl acetate–light petroleum, Whatman Partisil 10 M20 50 × 2.2 cm i.d. column, flow rate 13 mL min^{-1}, 1000 psi) from the mixture: IR (neat) ν_{max} 3050 (w), 2960 (s), 2930 (s), 1710 (s), 1085 (s), 1055 (s), 750 (s) cm^{-1}; ^1H NMR δ 0.79–0.88 (3 H, m, CH_3), 1.00–1.30 (6 H, m, 3 CH_2), 1.184 (9 H, s, *t*-Bu), 1.27–1.40 (1 H, m, CH_2), 1.45–1.57 (1 H, m, CH_2), 1.94 (1 H, dd, J = 18.3, 9.0 Hz, H5β), 2.15 (1 H, ddd, J = 18.5, 6.5, 1 Hz, H2α), 2.23 (1 H, dddd, J = 9.0, 8.0, 6.8, 6.8 Hz, H4α), 2.31 (1 H, dddd, J = 9.3, 6.8, 6.8, 3.5 Hz, H1′), 2.44 (1 H, ddd, J = 18.3, 8.0, 1 Hz, H5α), 2.52 (1 H, dd, J = 18.5, 6.5 Hz, H2β), 4.03 (1 H, ddd, J = 6.8, 6.5, 6.5 Hz, H3β), 6.25 (1 H, d, J = 15.3 Hz, H3′), 6.47 (1 H, dd, J = 15.3, 9.3 Hz, H2′), 7.45–7.64 (5 H, m, C_6H_5); MS m/e 374 (M^+ − O, 2), 373 (9), 319 (4), 318 (15), 317 (56), 109 (20), 57 (100), 55 (23); HRMS calcd for [$C_{23}H_{34}O_2S$ − OH] 373.2200, found 373.2172.

From the sulfoxide (Z/E 83:17) (617 mg, 2.61 mmol) and the enone (460 mg, 2.9 mmol) was obtained a 79:21 mixture of the diastereomers **26** and **25** as a colorless oil (471 mg, 70%). The major isomer was isolated by HPLC with 30:70 ethyl acetate–light petroleum: IR (neat) ν_{max} 3050 (w), 2960 (s), 2930 (s), 1710 (s), 1085 (s), 1055 (s), 750 (s) cm^{-1}; ^1H NMR δ 0.79–0.88 (3 H, m, CH_3), 1.11 (9 H, s, *t*-Bu), 1.1–1.3 (6 H, m, 3 CH_2), 1.3–1.55 (2 H, m, CH_2), 1.94 (1 H, dd, J = 17.7, 11.7 Hz, H5β), 2.16 (1 H, ddd, J = 18.6, 8.1, 1 Hz, H2α), 2.26 (1 H, dddd, J = 11.7, 8.4, 8.1, 4.2 Hz, H4α), 2.36 (1 H, ddd, J = 17.7, 8.4, 1 Hz, H5α) 2.57 (1 H, dd, J = 18.6, 7.2 Hz, H2β), 2.60 (1 H, dddd, J = 9.8, 9.8, 4.2, 4.2 Hz, H1′), 3.83 (1 H, ddd, J = 8.1, 8.1, 7.2 Hz, H3β), 6.27 (1 H, d, J = 15.1 Hz, H3′), 6.43 (1 H, dd, J = 15.1, 9.8 Hz, H2′), 7.46–7.67 (5 H, m, C_6H_5); MS m/e 374 (M^+ − O, 2), 373 (10), 319 (3), 318 (14), 317 (15), 219 (20), 109 (30), 59 (23), 57 (100), 55 (26); HRMS calcd for [$C_{23}H_{34}O_3S$ − O] 374.2278, found 374.2250.

(ii) 1-(Phenylsulfinyl)but-2-ene (6). From the sulfoxide (E/Z 80:20) (391 mg, 2.17 mmol) and the enone (326 mg, 2.17 mmol) was obtained a yellow oil. Purification first by flash chromatography with 40:60 ethyl acetate–light petroleum and then by HPLC with 30:70 ethyl acetate–light petroleum gave an 80:20 mixture of the (1′*RS*,2′*E*,3*SR*,4*RS*,R_SS_S) and (1′*RS*,2′*E*,3*RS*,4*SR*,S_SR_S) diastereomers **27** and **28** of *3-(1,1-dimethylethoxy)-4-[1′-methyl-3′-(phenylsulfinyl)prop-2′-enyl]cyclopentanone* as a pale yellow oil (360 mg, 64%): IR (neat) ν_{max} 2970 (s), 1745 (s), 1420 (m), 1330 (s), 1120 (s), 1070 (s), 800 (s), 760 (s) cm^{-1}; ^1H NMR (major isomer **14**) δ 1.05 (3 H, d, J = 6.8 Hz, CH_3), 1.19 (9 H, s, *t*-Bu), 1.91 (1 H, dd, J = 18.0, 9.5 Hz, H5β), 2.20 (1 H, ddd, J = 18.0, 7.5, 1.6 Hz, H5α), 2.20–2.41 (2 H, m, H2α, H4α), 2.58 (1 H, ddm, J = 18.0, 6.6 Hz, H2β), 2.60–2.69 (1 H, m, H1′), 3.99 (1 H, ddd, J = 7.2, 7.2, 6.6 Hz, H3β), 6.24 (1 H, dd, J = 15.2, 1.2 Hz, H3′), 6.64 (1 H, dd, J = 15.2, 7.2 Hz, H2′), 7.50–7.63 (5 H, m, C_6H_5); ^1H NMR (minor isomer **15**) δ 1.12 (3 H, d, J = 7.4 Hz, CH_3), 1.15 (9 H, s, *t*-Bu), 1.88 (1 H, dd, J = 18.0, 9.5 Hz, H5β), 2.1–2.7 (4 H, m, H2β, H2α, H4α, H5α), 2.72–2.81 (1 H, m, H1′), 3.94 (1 H, ddd, J = 7.6, 7.6, 7.6 Hz, H3β), 6.27 (1 H, dd, J = 15.2, 1.2 Hz, H3′), 6.56 (1 H, dd, J = 15.2, 8.2 Hz, H2′), 7.50–7.63 (5 H, m, C_6H_5); MS m/e 334 (M^+, 3), 319 (4), 317 (12), 262 (28), 261 (100), 207 (13), 193 (19), 163 (30), 131 (60), 109 (41), 59 (100); HRMS calcd for $C_{19}H_{26}O_3S$ 334.1602, found 334.1602.

(iii) 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). From the sulfoxide (341 mg, 1.76 mmol) and the enone (275 mg, 1.78 mmol) was obtained after flash chromatography with 40:60 ethyl acetate–light petroleum

(2'E,3RS,4SR,S$_S$R$_S$)-3-(1,1-dimethylethoxy)-4-[1',1'-dimethyl-3'-(phenylsulfinyl)prop-2'-enyl]cyclopentanone (**29**; 475 mg, 80%) as a pale yellow oil: IR (neat) ν_{max} 2950 (s), 1740 (s), 1460 (m), 1440 (s), 1380 (s), 1360 (s), 1180 (s), 1070 (s) cm^{-1}; ^{1}H NMR δ 1.118 (3 H, s, CH_3), 1.120 (3 H, s, CH_3), 1.21 (9 H, s, *t*-Bu), 1.75–2.80 (5 H, m, H2, H4, H5), 4.00–4.25 (1 H, m, H3), 6.19 (1 H, d, J = 15.4 Hz, H3'), 6.72 (1 H, d, J = 15.4 Hz, H2'), 7.45–7.75 (5 H, m, C_6H_5); MS *m/e* 250 (8), 208 (40), 109 (100), 125 (25); MS (CI) *m/e* 349 (P + 1), 363 (P + 15). Anal. Calcd for $C_{20}H_{28}O_3S$: C, 69.0; H, 8.1; S, 9.2. Found: C, 69.1; H, 8.3; S, 9.2.

A solution of tributylphosphine (272 mg, 1.32 mmol) and HMPA (227 mg, 1.35 mmol) in dry diethyl ether (10 mL) at room temperature under nitrogen was treated with a solution of iodine (150 mg, 1.2 mmol) in ether (5 mL). The resultant white suspension was treated with a solution of the conjugate addition product **29** (469 mg, 1.35 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. This was purified by flash chromatography with 15:85 ethyl acetate–light petroleum to give *(2'E,3RS,4SR)-3-(1,1-dimethylethoxy)-4-[1',1'-dimethyl-3'-(phenylthio)prop-2'-enyl]cyclopentanone* (**64**; 369 mg, 82): IR (neat) ν_{max} 2970 (s), 1740 (s), 1585 (w), 1470 (m), 1415 (m), 1210 (s), 1180 (m), 1110 (m) cm^{-1}; ^{1}H NMR δ 1.07 (3 H, s, CH_3), 1.14 (1 H, s, CH_3), 1.19 (9 H, s, *t*-Bu), 1.75–2.75 (5 H, m, H2, H3, H5), 3.98–4.20 (1 H, m, H4), 5.91 (1 H, d, J = 14.4 Hz, H3'), 6.09 (1 H, d, J = 14.4 Hz, H2'), 7.15–7.35 (5 H, m, C_6H_5); MS *m/e* 332 (M$^+$, 5), 258 (8), 276 (8), 178 (25), 177 (100), 109 (12), 59 (36), 57 (28), 41 (38). Anal. Calcd for $C_{20}H_{28}O_2S$: C, 72.3; H, 8.4; S, 9.6. Found C: 72.5; H, 8.3; S, 9.8.

Oxidation of the sulfide **64** (177 mg, 0.53 mmol) with *m*-chloroperoxybenzoic acid (110 mg, 0.53 mmol) in dichloromethane (20 mL) at −60 °C gave a yellow oil (195 mg) whose ^{1}H NMR spectrum (100 MHz) indicated that it consisted of a 1:1 mixture of the sulfoxides **29** and **65**. These were separated by HPLC with 30:70 ethyl acetate–light petroleum ether (Waters semipreparative μ-Porasil No. 2 column, 3 mL min^{-1}, 600 psi) to give first the sulfoxide **29** and then *(2'E,3RS,4SR,R$_S$S$_S$)-3-(1,1-dimethylethoxy)-4-[1',1'-dimethyl-3'-(phenylsulfinyl)prop-2'-enyl]-cyclopentanone* (**65**): IR ($CHCl_3$) ν_{max} 2970 (s), 1742 (s), 1445 (m), 1390 (m), 1366 (m), 1291 (m), 1260 (m), 1157 (m), 1085 (s), 1070 (m) 1022 (m) cm^{-1}; ^{1}H NMR δ 1.108 (3 H, s, CH_3), 1.149 (3 H, s, CH_3), 1.168 (9 H, s, *t*-Bu), 1.90–2.80 (5 H, m, H2, H4, H5), 3.98–4.25 (1 H, m, H3), 6.17 (1 H, d, J = 15.4 Hz, H3'), 6.67 (1 H, d, J = 15.5 Hz, H2'), 7.45–7.75 (5 H, m, C_6H_5); MS *m/e* 348 (2), 331 (2), 291 (2), 279 (15), 275 (22), 207 (37), 177 (39), 167 (19), 149 (5), 145 (100), 109 (50), 91 (18), 83 (21), 57 (84); HRMS calcd for $C_{20}H_{28}O_3S$ 348.1758, found 348.1759.

But-2-en-4-olide with (i) 1-(Phenylsulfinyl)oct-2-ene (4). From the sulfoxide (*E*/*Z* 85:15) (472 mg, 2.0 mmol) and the enone (172 mg, 2.0 mmol) was obtained after flash chromatography with 40:60 ethyl acetate–light petroleum an 83:17 mixture of the *(1'RS,2'E,3SR,R$_S$S$_S$)* and *(1'RS,2'E,3SR,S$_S$R$_S$)* diastereomers **30** and **31** of *[1'-pentyl-3'-(phenylsulfinyl)prop-2'-enyl]butan-4-olide* (536 mg, 83%) as a colorless oil. The major isomer was isolated by HPLC according to the foregoing conditions: IR (neat) ν_{max} 2920 (br), 1779 (s), 1208 (m), 1070 (m), 760 (m), 695 (m) cm^{-1}; ^{1}H NMR δ 0.79–0.85 (3 H, m, CH_3), 1.08–1.32 (6 H, m, 3 CH_2), 1.32–1.58 (2 H, m, CH_2), 2.23 (1 H, dd, J = 20.0, 12.0 Hz, H2β), 2.18–2.32 (1 H, m, H1'), 2.59 (1 H, dd, J = 20.0, 8.0 Hz, H2α), 2.55–2.65 (1 H, m, H3), 3.83 (1 H, dd, J = 9.6, 8.0 Hz, H4β), 4.23 (1 H, dd, J = 9.6, 8.0 Hz, H4α), 6.26–6.37 (2 H, m, H2', H3'), 7.44–7.66 (5 H, m, C_6H_5); MS *m/e* 320 (M$^+$, 17), 304 (16), 303 (18), 262 (30), 219 (22), 187 (100), 139 (22), 187 (78), 139 (22), 126 9270, 125 (28), 123 (26), 117 (50), 110 (45), 109 (82); HRMS calcd for $C_{18}H_{24}O_3S$ 320.1445, found 320.1442.

From the sulfoxide **4** (*Z*/*E* 83:17) and the enone (472 mg, 2.0 mmol) was obtained an 80:20 mixture of the diastereomers **31** and **30** as a colorless oil (514 mg, 80%). The major isomer was isolated by HPLC according to the above conditions: IR (neat) ν_{max} 3450 (b), 2930 (b), 1780 (s), 1740 (s), 1470 (s), 1450 (m), 1430 (s), 1280 (s), 1210 (s), 1115 (s), 1072 (s), 990 (m), 765 (m), 700 (s) cm^{-1}; ^{1}H NMR δ 0.78–0.88 (3 H, m, CH_3), 1.08–1.34 (6 H, m, 3 CH_2), 1.34–1.55 (2 H, m, CH_2), 2.19 (1 H, dd, J = 17.5, 9.8 Hz, H2β), 2.23–2.32 (1 H, m, H1'), 2.47 (1 H, dd, J = 17.5, 9.0 Hz, H2α), 2.61 (1 H, ddddd, J = 9.8, 9.0, 8.5, 8.0, 8.0 Hz, H3), 3.97 (1 H, dd, J = 9.6, 8.0 Hz, H4β), 4.41 (1 H, dd, J = 9.6, 8.0 Hz, H4α), 6.30–6.39 (2 H, m, H2', H3'), 7.44–7.66 (5 H, m, C_6H_5); MS *m/e* 320 (M$^+$, 10), 272 (24), 219 (12), 188 (15), 187 (100), 149 (15), 126 (32), 123 (25), 117 (62), 109 (100); HRMS calcd for $C_{18}H_{24}O_3S$ 320.1445, found 320.1445.

(ii) 1-(Methylsulfinyl)oct-2-ene (5). From the sulfoxide (*E*/*Z* 92:8) (348 mg, 2.0 mmol) and the enone (172 mg, 2.0 mmol) was obtained a pale yellow oil (410 mg), which after flash chromatography with 40:60 ethyl acetate–light petroleum gave *(1'RS,2'E,3RS,S$_S$R$_S$)-3-[3'-(methylsulfinyl)-1'-pentylprop-2'-enyl]butan-4-olide* (**32**) as a colorless oil (325 mg, 63%) containing 8% of a second diastereomer: IR (neat) ν_{max} 3400 (b), 2850 (br), 1780 (s), 1620 (m), 1460 (m), 1420 (m), 1370 (m), 1350 (m), 1170 (s), 960 (s), 840 (m), 790 (m), 720 (w), 680 (m) cm^{-1}; ^{1}H NMR δ 0.84–0.93 (3 H, m, CH_3), 1.13–1.43 (6 H, m, 3 CH_2), 1.48–1.58 (2 H, m, CH_2), 2.25–2.36 (1 H, m, H1'), 2.30 (1 H, dd, J = 16.8, 7.6 Hz, H2β), 2.61 (1 H, ddddd, J = 8.2, 7.6, 7.6, 7.6, 7.6 Hz, H3), 2.63 (3 H, s, CH_3), 2.75 (1 H, dd, J = 16.8, 7.6 Hz, H3), 3.95 (1 H, dd, J = 9.6, 7.6 Hz, H4β), 4.35 (1 H, dd, J = 9.6, 7.6 Hz, H4α), 6.20 (1 H, dd, J = 15.2, 9.8 Hz, H2), 6.38 (1 H, d, J = 15.2 Hz, H3'); MS *m/e* 258 (M$^+$, 5), 241 (45), 173 (58), 157 (22), 152 (24), 135 (22), 123 (15), 109 (33), 95 (35), 93 (27), 87 (30), 85 (24), 81 (45), 79 (38); HRMS calcd for $C_{13}H_{22}O_3S$ 258.1289, found 258.1272.

(iii) 1-(Phenylsulfinyl)but-2-ene (6). The sulfoxide (*E*/*Z* 76:24) (387 mg, 2.15 mmol) and the enone (183 mg, 2.17 mmol) after flash chromatography with 40:60 ethyl acetate–light petroleum ether gave a 75:25 mixture of the *(1'RS,2'E,3RS,R$_S$S$_S$)* and *(1'RS,2'E,3SR,S$_S$R$_S$)* diastereomers **33** and **34** of *[1'-methyl-3'-(phenylsulfinyl)prop-2'-enyl]butan-4-olide* as a pale yellow oil (507 mg, 71%). The major isomer **33** was isolated by HPLC with 3:97 ethyl acetate–light petroleum (Waters semipreparative μ-Porasil No. 2 column, 30 cm × 7.8 mm i.d. column, flow rate 3 mL min^{-1}, 600 psi): IR (neat) ν_{max} 2960 (s), 1780 (s), 1630 (w), 1340 (w), 1210 (s), 1110 (w), 1060 (s), 1030 (s), 1000 (m), 800 (s), 730 (s), 700 (s), cm^{-1}; ^{1}H NMR δ 1.09 (3 H, d, J = 6.84 Hz, CH_3), 2.21 (1 H, dd, J = 16.6, 7.5 Hz, H2β), 2.34–2.44 (1 H, m, H3α), 2.47–2.59 (1 H, m, H1'), 2.58 (1 H, dd, J = 16.6, 8.6 Hz, H2α), 3.87 (1 H, dd, J = 9.3, 7.2 Hz, H4β), 4.28 (1 H, dd, J = 9.3, 7.2 Hz, H4α), 6.26 (1 H, dd, J = 15.0, 0.7 Hz, H3'), 6.38 (1 H, dd, J = 15.0, 8.2 Hz, H2'), 7.4–7.6 (5 H, m, C_6H_5); MS *m/e* 264 (M$^+$, 4), 216 (22), 163 (10), 131 (100), 109 (60). Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.6; H, 6.1; S, 12.1. Found: C, 63.7; H, 6.1; S, 11.7.

The minor isomer **34** could not be separated from the major diastereomer. ^{1}H NMR δ 1.07 (3 H, d, J = 6.9 Hz, CH_3), 2.19–2.29 (1 H, m, H2β), 2.43–2.77 (3 H, m, H2α, H3α, H1'), 4.01 (1 H, dd, J = 9.1, 7.2 Hz, H4β), 4.42 (1 H, dd, J = 9.1, 7.2 Hz, H4α), 6.28 (1 H, dd, J = 15.0, 0.7 Hz, H3'), 6.43 (1 H, dd, J = 15.0, 8.2 Hz, H2'), 7.47–7.60 (5 H, m, C_6H_5).

(iv) 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). From the sulfoxide (395 mg, 2.04 mmol) and the enone (183 mg, 2.1 mmol) was obtained after flash chromatography with 25:75 ethyl acetate–chloroform *(2'E,3RS,R$_S$S$_S$)-3-[1',1'-dimethyl-3'-(phenylsulfinyl)prop-2'-enyl]butan-4-olide* (**35**; 463 mg, 82%) as a colorless oil: IR (neat) ν_{max} 2950 (s), 1780 (s) 1400 (s), 1210 (s), 1100 (s), 1050 (s) cm^{-1}; ^{1}H NMR δ 1.08 (3 H, s, CH_3), 1.10 (3 H, s, CH_3), 2.30 (1 H, dd, J = 17.6, 8.0 Hz, H2β), 2.51 (1 H, dd, J = 17.6, 9.2 Hz, H2α), 2.61 (1 H, dddd, J = 9.2, 8.0, 8.0, 6.8 Hz, H3α), 4.05 (1 H, dd, J = 9.6, 6.8 Hz, H4β), 4.31 (1 H, dd, J = 9.6, 8.0 Hz, H4α), 6.25 (1 H, d, J = 15.2 Hz, H3'), 6.51 (1 H, d, J = 15.2 Hz, H2'), 7.50–7.65 (5 H, m, C_6H_5); MS *m/e* 278 (M$^+$, 5), 262 (2), 230 (6), 193 (12), 177 (20), 145 (100), 109 (45). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.8; H, 6.5; S, 11.5. Found: C, 64.6; H, 6.5; S, 11.7.

Cyclopent-2-enone with (i) 1-(Phenylsulfinyl)but-2-ene (6). From the sulfoxide (*E*/*Z* 80:20) (207 mg, 1.147 mmol) and the enone (94 mg, 1.147 mmol) was obtained a colorless oil (278 mg). Optimum yields were provided by saturating the quenched reaction mixture with sodium chloride prior to extraction with diethyl ether. The oil was submitted to flash chromatography with ethyl acetate–light petroleum ether (65:35 graded to 80:20) to give an inseparable 80:20 mixture of the *(1'RS,2'E,3RS,R$_S$S$_S$)* and *(1'RS,2'E,3Sr,S$_S$R$_S$)* diastereomers **36** and **37** of *(E)-[1'-methyl-3'-(phenylsulfinyl)-prop-2'-enyl]cyclopentanone* as a colorless viscous oil (217 mg, 72%): IR (neat) ν_{max} 3025 (w), 2940 (m), 2852 (w), 1730 (s, C=O), 1465 (w), 1437 (m), 1397 (m), 1365 (w) 1270 (w), 1230 (w), 1159 (s), 1080 (s), 1045 (s), 1013 (w), 964 (m), 892 (w), 742 (s), 681 (s) cm^{-1}; ^{1}H NMR (100 MHz) (* denotes minor isomer) δ 1.12, 1.14* (3 H, d, J = 6 Hz, CH_3), 1.38–2.59 (8 H, m, H2, H3, H4, H5, H1'), 6.20*, 6.32 (1 H, d, J = 15.3 Hz, H3'), 6.43*, 6.55 (1 H, dd, J = 15.3, 7.4 Hz, H2'), 7.44–7.76 (5 H, m, C_6H_5); MS *m/e* 262 (M$^+$, 6), 248 (M − O, 6), 163 (44), 131 (94), 125 (20), 110 (31), 109 (60), 83 (29), 78 (28), 77 (44), 69 (47), 67 (21), 65 (28), 60 (22), 55 (100), 53 (28), 51 (37), 45 (34), 43 (78), 41 (44) 39 (42), 32 (21), 29 (32), 28 (100); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1027.

The lithiated sulfoxide (222 mg, 1.23 mmol) was generated at −70 °C and then treated at −10 °C with the enone (101 mg, 1.23 mmol) to give the above diastereomers (254 mg, 79%) in the same ratio.

(ii) (*tert*-Butylsulfinyl)but-2-ene (7). The sulfoxide (*E*/*Z* 94:6) (216 mg, 1.35 mmol) and the enone (111 mg, 1.35 mmol) at −10 °C gave after saturation of the quenched reaction mixture with sodium chloride prior to extraction with diethyl ether a pale yellow viscous oil (340 mg). This was chromatographed with ethyl acetate to give

(1'RS,2'E,3RS,RSSS)-3-[3'-[(1,1-dimethylethyl)sulfinyl]-1'-methylprop-2'-enyl]cyclopentanone (**38**) as a colorless viscous oil (231 mg, 71%) containing 7% of a second diastereomer, which could not be removed: IR (neat) ν_{max} 2950 (s), 2860 (sh), 1735 (s, C=O), 1610(w), 1458 (m), 1402 (m), 1365 (m), 1280 (w), 1240 (w), 1160 (s), 1090 (w), 1050 (s), 972 (m), 920 (w), 805 (m), 725 cm^{-1}; ^1H NMR δ 1.76 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, 1'-CH_3), 1.86 (9 H, s, *t*-Bu), 2.11–2.24 (1 H, m, H4β), 2.51 (1 H, ddd, J = 18, 10.8, 1.4 Hz, H2β), 2.71–2.85 (3 H, m), 2.89–3.08 (3 H, m, H2α, H1', H3, H4α, H5α, H5β), 6.825 (1 H, dd, J = 15.3, 0.7 Hz, H3'), 7.01 (1 H, dd, J = 15.3, 8.6 Hz, H2'); MS (CI) *m/e* 485 (2M + 1, 14), 243 (M + 1, 87), 103 (9), 83 (11), 57 (100), 55 (19), 53 (9), 41 (29), 39 (20), 29 (28). Anal. Calcd for $C_{13}H_{22}O_2S$: C, 64.4; H, 9.2. Found: C, 64.3; H, 9.4.

Repetition of the conjugate addition at −70 °C did not alter the ratio of the diastereomers. Addition of a solution of the enone (232 mg, 2.84 mmol) in THF (5 mL) containing anhydrous lithium bromide (287 mg, 3.2 mmol) to the lithiated sulfoxide (from the sulfoxide, 413 mg, 2.58 mmol) at −70 °C gave the product **38** (550 mg, 80%).

(iii) 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). The sulfoxide (397 mg, 2.05 mmol) with the enone (185 mg, 2.25 mmol) after flash chromatography with 40:60 ethyl acetate–light petroleum ether gave *(2'E,3RS,RSSS)-3-[1',1'-dimethyl-3'-(phenylsulfinyl)prop-2'-enyl]-cyclopentanone* (**39**; 310 mg, 85%) as a colorless oil, which slowly became a white solid, mp 55–59 °C, containing 20% of a second diastereomer, assumed to be the anti product. The presence of the two diastereomers could only be established through use of 400-MHz ^1H NMR spectroscopy; they had identical HPLC retention times under a variety of conditions. Similar results were obtained when the enone was added at −30 °C and the reaction mixture quenched at −20 °C. The reaction was also carried out in diethyl ether at −70 and −40 °C to give the diastereomers in 64–72% yields: IR (neat) ν_{max} 2950 (s), 1740 (s), 1440 (m), 1420 (w), 1160 (m), 1080 (m), 1040 (s) cm^{-1}; ^1H NMR (major isomer) δ 1.11 (6 H, s, 2 CH_3) 1.56–2.37 (7 H, m, H2, H3, H4, H5), 6.20 (1 H, d, J = 15.4 Hz, H3'), 6.60 (1 H, d, J = 15.4 Hz, H2'), 7.47–7.65, m, C_6H_5; MS *m/e* 276 (M^+, 6), 260 (5), 193 (20), 178 (10), 177 (70), 145 (100), 139 (20), 126 (30), 109 (50). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.6; H, 7.3. Found: C, 69.3; H, 7.7.

(iv) 1-(*tert*-Butylsulfinyl)-3-methylbut-2-ene (9). The sulfoxide (385 mg, 2.14 mmol) and the enone (216 mg, 2.24 mmol) gave after flash chromatography with 60:40 ethyl acetate–light petroleum ether *(2'E,3RS,RSSS)-3-[1',1'-dimethyl-3'-[(1,1-dimethylethyl)sulfinyl]prop-2'-enyl]cyclopentanone* (**40**; 330 mg, 57%) as prisms, mp 72–74 °C from ethyl acetate–light petroleum. When the anion was generated at −60 °C, treated with the enone at −20 °C, and quenched at −10 °C, **40** was obtained in 80% yield: IR (neat) ν_{max} 2865 (br, s), 1735 (s), 1460 (s), 1410 (s), 1190 (s), 1140 (s), 1040 (s) cm^{-1}; ^1H NMR δ 1.136 (3 H, s, CH_3), 1.139 (3 H, s, CH_3), 1.225 (9 H, s, *t*-Bu), 1.63 (1 H, ddm, J = 10.0, 8.25 Hz, H4β), 1.90–2.39 (5 H, m, H2α, H2β, H3α, H4α, H5α), 2.34 (1 H, ddm, J = 18.6, 8.25 Hz, H5β), 6.10 (1 H, d, J = 15.4 Hz, H3'), 6.43 (1 H, d, J = 15.4 Hz, H2'); MS *m/e* 256 (M^+, 1), 240 (1), 200 (1), 125 (10), 109 (100), 101 (30), 69 (25), 57 (90); MS (CI) *m/e* 257 (P + 1), 513 (2P + 1). Anal. Calcd for $C_{14}H_{24}O_2S$: C, 65.6; H, 9.4. Found: C, 66.0; H, 9.8.

(v) 5-(Phenylsulfinyl)pent-3-en-1-ol (12). The sulfoxide (*E*/*Z* 85:15) (427 mg, 2.03 mmol) and the enone (190 mg, 2.3 mmol) gave after flash chromatography with ethyl acetate *(1'RS,2'E,3RS,RSSS)-3-[1'-(2''-hydroxyethyl)-3'-(phenylsulfinyl)prop-2'-enyl]cyclopentanone* (**41**) as a colorless oil (530 mg, 90%) containing 15% of a second diastereomer. This was submitted to HPLC (ethyl acetate, Waters semipreparative μ-Porasil No. 2 column, 3 mL min^{-1}, 400 psi) to give the major isomer (350 mg, 58%) as needles, mp 85–88 °C from diethyl ether–ethyl acetate: IR ($CHCl_3$) ν_{max} 3621 (s), 3450 (s, OH), 3010 (s), 2976 (s), 2895, (m), 1740 (s), 1445 (m), 1402 (m), 1242 (m), 1084 (m), 1045 (s), 677 (m) cm^{-1}; ^1H NMR δ 1.41–2.47 (10 H, m), 1.79 (1 H, s, OH), 3.54 (1 H, ddd, J = 10.7, 8.9, 5.6 Hz, H2''), 3.67 (1 H, ddd, J = 10.7, 8.9, 5.6 Hz, H2''), 6.32 (1 H, d, J = 15.1 Hz, H3'), 6.41 (1 H, dd, J = 15.1, 9.5 Hz, H2'), 7.47–7.65 (5 H, m, C_6H_5); MS *m/e* 292 (M^+, 2), 275 (28), 193 (5), 167 (46), 165 (10), 153 (14), 126 (48), 109 (43), 83 (68), 55 (100). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.8; H, 6.9. Found: C, 66.1; H, 7.2.

(vi) 5-(Phenylsulfinyl)pent-3-enyl Dimethyl(1,1-dimethylethyl)silyl Ether (13). From the sulfoxide (*E*/*Z* 85:15) (477 mg, 1.47 mmol) and the enone (133 mg, 1.62 mmol) was obtained after flash chromtography with 35:65 ethyl acetate–light petroleum an 85:15 mixture of diastereomers of the conjugate addition product. The mixture was submitted to HPLC (35:65 ethyl acetate:light petroleum, Brownlee column, SI 100, 5 μm, flow rate 1.5 mL min^{-1}, 500 psi) to give *(1'RS,2'E,3RS,RSSS)-3-[1'-[2''-[dimethyl(1,1-dimethylethyl)siloxy]ethyl]-3'-(phenylsulfinyl)-prop-2'-enyl]cyclopentanone* (**42**) as a clear viscous oil (450 mg, 73%): IR (neat) ν_{max} 2940 (s), 2840 (sh), 1730 (s), 1470 (m), 1420 (m), 1400 (m), 1380 (m), 1250 (s), 1180 (s), 1140 (s), 970 (m), 940 (m), 830 (s), 770 (s), 740 (m), 690 (m) cm^{-1}; ^1H NMR δ 0.09 (6 H, s, 2 CH_3), 0.95 (9 H, s, *t*-Bu), 1.24–2.54 (10 H, m), 3.30–3.58 (2 H, m, H2''), 6.19–6.30 (2 H, m, H2',H3'), 7.14–7.64 (5 H, m, C_6H_5); MS *m/e* 392 (3), 391 (3), 390 (5), 375 (6), 349 (100), 333 (100), 288 (12), 276 (10). Anal. Calcd for $C_{22}H_{34}O_3SSi$: C, 65.0; H, 8.37 Found: C, 64.8; H, 8.8.

2,2-Dimethyl-3(2*H*)-furanone with 3-[(4-Methylphenyl)sulfinyl]prop-1-ene (10). The sulfoxide (579 mg, 3.22 mmol) and the enone (396 mg, 3.54 mmol) gave after flash chromatography with 35:65 ethyl acetate–light petroleum *(2'E,4RS,SSRS)-dihydro-2,2-dimethyl-5-[[(4-methylphenyl)sulfinyl]prop-2'-enyl]-3(2H)-furanone* (**43**) as a colorless oil (670 mg, 71%) containing 17% of a second diastereomer: IR (neat) ν_{max} 2980 (s), 1760 (s), 1600 (w)8, 1480 (m), 1380 (s), 1180 (s), 1110 (s), 1080 (m), 1040 (s), 1010 (m), 960 (m), 810 (m) cm^{-1}; ^1H NMR (major isomer) δ 1.20 (3 H, s, CH_3), 1.27 (3 H, s, CH_3), 2.25 (1 H, dd, J = 18.2, 9.9 Hz, H4β), 2.42 (3 H, s, CH_3), 2.56 (1 H, dd, J = 18.2, 5.8 Hz, 4α), 2.61 (2 H, m, H1'), 4.32 (1 H, dddd, J = 9.9, 5.8, 5.8, 5.8 Hz, H3α), 6.36 (1 H, ddd, J = 15.2, 1.3, 1.3 Hz, H3'), 6.61 (1 H, ddd, J = 15.2, 6.9, 6.9 Hz, H2'), 7.32–7.51 (4 H, m, C_6H_4); MS *m/e* 292 (M^+, 14) 276 (34), 244 (40), 180 (12), 164 (33), 163 (100). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.8; H, 6.9. Found: C, 65.6; H, 7.0.

3-Methylcyclopent-2-enone with (i) 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). The sulfoxide (333 mg, 1.72 mmol) and the enone (182 mg, 1.89 mmol) gave a pale yellow oil (550 mg), which upon standing deposited fine white needles. The crystals were filtered, washed with cold diethyl ether, and dried to give *1-[3'-methyl-1'-(phenylsulfinyl)but-2'-enyl]-3-methylcyclopent-2-en-1-ol* (**44**) as white needles (460 mg, 83%), mp 84–87 °C (dec). A solution of the solid in $CDCl_3$ according to ^1H NMR analysis contained four diastereomers; the ratio of these in the solution changed with time. After 10 min of dissolving the above compound in acid-free $CDCl_3$, the ratio of the four isomers was 5:10:27:58, at 35 min the ratio had changed to 8.5:16:38.5:37, and after 4.5 h the ratio was 12:22:49.5:16.5. The mixture decomposed during attempted chromatography or recrystallization: IR ν_{max} ($CHCl_3$) 3660 (m), 3600 (m), 3350 (s), 2940 (brs), 2400 (s), 1660 (m), 1600 (w), 1410 (brs), 1260 (s), 1150 (s), 1000 (s), 910 (m) cm^{-1}; ^1H NMR (major isomer at 10 min) δ 0.830 (3 H, d, J = 1.2 Hz, CH_3), 1.626 (3 H, d, J = 1.24 Hz, CH_3), 1.787 (3 H, d, J = 1.0 Hz, CH_3), 1.92–2.68 (4 H, m, H4, H5), 3.27 (1 H, s, OH), 3.30 (1 H, d, J = 11.2 Hz, H1'), 5.34 (1 H, dm, J = 11.2 Hz, H2'), 5.57 (1 H, m, J = 1.5 Hz, H2), 7.40–7.70 (5 H, m, C_6H_5); MS *m/e* 292 (M^+ + 2, 10), 250 (12), 234 (11), 218 (10), 186 (77), 147 (60), 146 (72), 131 (100).

(ii) 3-[(4-Methylphenyl)sulfinyl]prop-1-ene (10). The sulfoxide (446 mg, 2.48 mmol) and the enone (267 mg, 2.78 mmol) after flash chromatography with 45:55 ethyl acetate–light petroleum gave first unreacted sulfoxide (77 mg) and then *(2'E,3RS,SSRS)-3-methyl-3-[3'-[(4-methylphenyl)sulfinyl]prop-2'-enyl]cyclopentanone* (**45**; 490 mg, 71%) as a colorless oil. When HMPA was used in the reaction, the products was obtained in 59% yield, together with a considerable amount of starting material: IR (neat) ν_{max} 2960 (s), 1740 (s), 1610 (w), 1490 (w), 1450 (m), 1410 (m), 1160 (m), 1080 (m), 1140 (s), 960 (m), 810 (m) cm^{-1}; ^1H NMR δ 1.11 (3 H, s, CH_3), 1.77–1.95 (2 H, m, H4α, H4β), 2.05 (1 H, dd, J = 18.0, 1 Hz, H2β), 2.12 (1 H, d, J = 18.0 Hz, H2α), 2.25–2.35 (4 H, m, H5α, H5β, H1'), 2.41 (3 H, s, CH_3), 6.28 (1 H, dt, J = 15.0, 1.25, 1.3 Hz, H3'), 6.58 (1 H, ddd, J = 15.0, 7.5, 7.5 Hz, H2'), 7.30–7.55 (5 H, m, C_6H_5); MS *m/e* 276 (M^+, 4), 260 (10), 228 (30), 163 (37), 131 (100), 123 (26), 97 (20), 91 (30). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.6; H, 7.2. Found: C, 69.4; H, 7.2.

Cyclohex-2-enone with (i) 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). From the sulfoxide (378 mg, 1.95 mmol) and the enone (203 mg, 2.15 mmol) was obtained a yellow oil, which after flash chromatography with 30:70 ethyl acetate–light petroleum gave first *(2'E,3RS,SSRS)-3-[1',1'-dimethyl-3'-(phenylsulfinyl)prop-2'-enyl]cyclohexanone* (**46**; 250 mg, 44%) as a colorless oil: IR (neat) ν_{max} 2980 (s), 1710 (s), 1480 (m), 1450 (m), 1100 (m), 1060 (s) cm^{-1}; ^1H NMR δ 1.07 (6 H, s, CH_3), 1.25–2.43 (7 H, m, H2, H3, H4, H5, H6), 6.16 (1 H, d, J = 15.5 Hz, H3'), 6.55 (1 H, d, J = 15.5 Hz, H2'), 7.47–7.65 (5 H, m, C_6H_5); MS *m/e* 290 (M^+, 6), 274 (2), 193 (10), 177 (100), 164 (18), 145 (60), 109 (50). Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.3; H, 7.9. Found: C, 70.0; H, 7.9.

The next fraction eluted was a mixture of four diastereomers of the carbonyl addition product **47** obtained initially as a yellow oil (200 mg, 35%), which could not be resolved into its components by HPLC and which upon removal of traces of solvent became a white solid. This was recrystallized from ethyl acetate–light petroleum to give an unstable solid as needles, mp 107–112 °C. A $CDCl_3$ solution of the solid contained a 32:30:28:20 mixture of diastereomers of *1-[3'-methyl-1'(phenylsulfinyl)but-2'-enyl]cyclohex-2-en-1-ol*: IR ($CHCl_3$) ν_{max} 3600 (sh), 3400 (br, s, OH), 1450 (s), 1380 (m), 1090 (s), 1010 (s) cm^{-1}; ^1H NMR (major isomer) δ 0.78 (3 H, d, J = 1.3 Hz, CH_3), 1.644 (3 H, d, J = 1.3 Hz, CH_3), 1.6–2.5 (6 H, m), 3.142 (1 H, d, J = 11.2 Hz, H1'), 4.12 (1

H, s, OH), 4.411 (1 H, d, J = 11.2 Hz, H2′), 5.313 (1 H, dm, $J \simeq 10$ Hz, H2), 5.88–5.98 (1 H, m, H3), 7.4–7.70 (5 H, m, C_6H_5); MS m/e 250 (6), 218 (4) 165 (12), 164 (22), 148 (20), 147 (19), 146 (18), 133 (13), 131 (24), 125 (57), 121 (20), 110 (33), 109 (50), 108 (35), 105 (30), 78 (100), 77 (90), MS (CI) m/e 291 (P + 1). Because of the instability of the compounds, satisfactory combustion analyses could not be obtained.

When the above reaction was performed in the presence of HMPA (1 equiv) the same two regioisomeric products **46** and **47** were again obtained in the ratio 60:40 (77%). Addition of the cyclohexenone in THF containing 2 equiv of lithium bromide to the lithiated sulfoxide gave an 85% yield of the products in a ratio of 65:35.

(ii) 3-(Phenylsulfinyl)prop-1-ene (11). The sulfoxide (387 mg, 2.33 mmol) and the enone (246 mg, mg, 2.56 mmol) gave a yellow oil, which after radial chromatography with 1:1 ethyl acetate–light petroleum gave two fractions. The less polar fraction (63 mg, 10%) was an inseparable, approximately equimolar mixture of four diastereomers of *[1′-(phenylsulfinyl)prop-2′-enyl]cyclohex-2-en-1-ol* (**49**; 63 mg, 10%), an unstable white amorphous solid: IR ($CHCl_3$) ν_{max} 3600 (sh), 3390–3430 (brs), 2936 (s), 2869 (sh), 1687 (w), 1478 (w), 1444 (s), 1327 (w), 1146 (m), 1136 (m), 1085 (s), 1059 (s), 1020 (s), 998 (s), 935 (m), cm^{-1}; ^1H NMR δ 2.18–1.55 (6 H, m), 2.98 (brs, OH), 3.46 (brs, OH), 2.91 (1 H, d, J = 10.3 Hz, H1′), 2.99 (1 H, d, J = 10.3 Hz, H1′), 3.50 (1 H, d, J = 10.7 Hz, H1′), 3.57 (1 H, d, J = 10.5 Hz, H1′), 4.51 (1 H, ddd, J = 17.2, 1.8, 0.6 Hz, H3′*E*), 4.53 (1 H, ddd, J = 17.2, 1.8, 0.6 Hz, H3′*E*), 4.57 (1 H, ddd, J = 17.2, 1.3, 0.5 Hz, H3′*E*), 4.64 (1 H, ddd, J = 17.2, 1.3, 0.5 Hz, H3′*E*), 5.11 (1 H, dd, J = 10.3, 1.3 Hz, H3′*Z*), 5.15 (1 H, dd, J = 10.5, 1.8 Hz, H3′*Z*), 5.17 (1 H, dd, J = 10.3, 1.3 Hz, H3′*Z*), 5.19 (1 H, dd, J = 10.3, 1.8 Hz, H3′*Z*), 5.40–5.56 (1 H, m, H2′ two isomers), 5.80–6.03 (m, H2′ two isomers), 7.43–7.80 (5 H, m, C_6H_5); MS m/e 250 (9), 256 (1), 218 (3), 196 (1), 166 (5), 149 (7), 137 (50), 127 (50), 125 (60), 119 (42), 109 (48), 77 (100).

The more polar fraction was submitted to HPLC with 60:40 ethyl acetate–light petroleum (Whatman 10 M20 column, flow rate 13 mL min^{-1}, 800 psi) to give three fractions in the approximate ratio of 65:20:15. The least polar, most abundant fraction (R_f 93 min) was an inseparable 62:38 mixture of diastereomers of *3-[3′-(phenylsulfinyl)-prop-2′-enyl]cyclohexanone* (**48**; 362 mg, 59%): IR (neat) ν_{max} 2937 (s), 1708 (s), 1443 (s), 1084 (s), 1043 (s), 1022 (m), 968 (m), 749 (s), 690 (m) cm^{-1}; ^1H NMR (* denotes minor isomer) δ 1.25–2.37 (11 H, m), 6.20, 6.21* (1 H, ddd, J = 15.1, 1.2, 1.2 Hz, H3′), 6.467, 6.474* (1 H, ddd, J = 15.1, 7.6, 7.6 Hz, H2′), 7.38–7.58 (5 H, m, C_6H_5); MS m/e 262 (M^+, 5), 246 (7), 214 (100), 196 (8), 156 (40), 149 (55), 147 (10), 136 (16), 123 (45), 117 (60), 109 (45), 97 (61), 95 (42), 91 (20), 83 (18), 77 (23); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1027.

The next fraction to be eluted (R_f 102 min) was *1-[3′-(phenylsulfinyl)prop-2′-enyl]cyclohex-2-en-1-ol* (**50**; 68 mg, 11%) as a colorless oil: IR (neat) ν_{max} 3370 (s), 2934 (s), 1443 (s), 1083 (s), 1033 (s), 1021 (s), 997 (m), 980 (m), 970 (m), 750 (m), 690 (m) cm^{-1}; ^1H NMR δ 1.18–2.40 (6 H, m), 2.42 (2 H, d, J = 7.4 Hz, H1′), 2.80 (1 H, s, OH), 5.60 (1 H, dm, J = 9.9 Hz, H2), 5.82 (1 H, ddd, J = 9.9, 4.5, 3.1 Hz, H3), 6.29 (1 H, dt, J = 15.1, 1.1 Hz, H3′), 6.67 (1 H, dt, J = 15.1, 7.4 Hz, H2′), 7.39–7.67 (5 H, m, C_6H_5); MS m/e 262 (M^+, 2), 245 (4), 166 (71), 149 (85), 134 (10), 117 (42), 109 (28), 97 (100), 91 (22), 79 (38), 78 (35), 77 (45); HRMS calcd for $C_{15}H_{18}O_2S$ 262.1027, found 262.1024.

The third and least abundant fraction eluted (R_t 120 min) was identified as a second diastereomer of *1-[3′-(phenylsulfinyl)prop-2′-enyl]-cyclohex-2-en-1-ol* (**50**; 53 mg, 9%) on the basis of the following data: IR (neat) ν_{max} 3380 (s), 2934 (s), 1443 (m), 1084 (s), 1028 (s), 1019 (s), 986 (m), 746 (m), 689 (m) cm^{-1}; ^1H NMR δ 1.5–2.5 (7 H, m), 2.75 (1 H, ddd, J = 14.0, 7.0, 0.9 Hz, H1′), 2.92 (1 H, ddd, J = 14.0, 7.0, 0.5 Hz, H1′), 5.68 (1 H, dm, J = 9.9 Hz, H2′), 5.89 (1 H, ddd, J = 9.9, 4.3, 3.1 Hz, H3), 6.33–6.43 (2 H, m, H2′, H3′), 7.40–7.70 (5 H, m, C_6H_5); MS m/e 245 (2), 244 (<1), 166 (68), 149 (100), 134 (10), 125 (8), 117 (20), 109 (10), 97 (64), 91 (12), 77 (13); HRMS calcd for [$C_{15}H_{18}O_2S$ – H_2O] 244.0922, found 244.0923.

Cyclohept-2-enone with 3-Methyl-1-(phenylsulfinyl)but-2-ene (8). From the sulfoxide (476 mg, 2.45 mmol) and the enone (321 mg, 2.9 mmol) at −70 °C was obtained a yellow oil (690 mg), which became a crystalline solid after 24 h at 4 °C. Although this could be recrystallized from ethyl acetate to give *1-[3′-methyl-1′-(phenylsulfinyl)but-2′-enyl]-cyclohept-2-en-1-ol* (**51**) as crystalline aggregates of prisms, mp 109–112 °C (570 mg, 77%), a solution in $CDCl_3$ consisted of a 36:30:20:14 mixture of diastereomers. Attempted separation by HPLC was unsuccessful since the isomers underwent equilibration under these conditions: IR (neat) ν_{max} 3360 (brs), 2920 (s), 1660 (m), 1450 (s), 1380 (m), 1250 (w), 1220 (w), 1170 (w), 1080 (s), 1030 (s), 910 (m), 850 (m), 730 (s) cm^{-1}; ^1H NMR (major diastereomer) δ 0.77 (3 H, d, J = 1.4 Hz, CH_3), 1.65 (3 H, d, J = 1.4 Hz, CH_3), 1.35–2.45 (8 H, m), 3.65 (1 H, d, J = 11.3 Hz, H1′), 4.1 (1 H, s, OH), 4.96 (1 H, dm, J = 11.3 Hz, H2′), 6.11 (1 H, ddd, J = 11.3, 6.7, 5.9 Hz, H3), 6.29 (1 H, dm, J = 11.3 Hz, H2), 7.40–7.70 (5 H, m, C_6H_5); MS (CI) m/e 305 (P + 1). Anal. Calcd for $C_{18}H_{24}O_2S$: C, 71.05; H, 7.9; S, 10.5. Found: C, 71.0; H, 7.9; S, 11.0.

4,4a,5,6,7,8-Hexahydro-4a-methyl-2(3*H*)-naphthalenone with 1-(Phenylsulfinyl)prop-2-ene (11). The sulfoxide (428 mg, 2.57 mmol) and the enone (529 mg, 3.23 mmol) gave after flash chromatography with 40:60 ethyl acetate–light petroleum a 70:30 mixture of two diastereomers of *(2′E)-4,4a,5,6,7,8-hexahydro-4a-methyl-2-[3′-(phenylsulfinyl)prop-2-enyl]-2(3H)-naphthalenol* (**52**) as a colorless oil (500 mg, 53%): IR (neat) ν_{max} 3350 (br, s), 2930 (s), 2850 (m), 1700 (w), 1030 (s) cm^{-1}; ^1H NMR (90 MHz) (major diastereomer) δ 1.08 (3 H, s, CH_3), 0.8–2.8 (14 H, m), 5.17 (1 H, s, H1), 6.24 (1 H, d, J = 15.8 Hz, H3′), 6.68 (1 H, ddd, J = 15.8, 6.8, 6.8 Hz, H2′) 7.3–7.6 (5 H, m, C_6H_5); MS m/e 314 (M^+ − 16, 5), 313 (18), 297 (10), 264 (20), 165 (40), 166 (37), 149 (100). Anal. Calcd for $C_{20}H_{26}O_2S$: C, 72.7; H, 7.9. Found: C, 72.9; H, 7.9. ^1H NMR and TLC analyses of the crude product mixture also indicated the presence both of starting compounds and substantial amounts of a less polar unidentified product, which decomposed upon attempted isolation.

(2) Lithiated Allylic Phosphine Oxides and Phosphonates. General Method. This was as for the allylic sulfoxides except that butyllithium was used for the deprotonation. It was added to the solution of the phosphine oxide (1–3 mmol) in THF until the first permanent appearance of the red color of the carbanion. Thereupon, 1.1 equiv of the butyllithium was added. For the phosphonates, whose carbanions are less intensely colored, 1.1 equiv of butyllithium was added to the solutions after the first permanent appearance of the red color of an added indicator, 2,2′-bipyridyl.

4-*tert*-Butoxycyclopent-2-enone with Oct-2-enyldiphenylphosphine oxide (14). From the phosphine oxide (*E*/*Z* 95:5) (730 mg, 2.34 mmol) and the enone (387 mg, 2.52 mmol) was obtained after flash chromatography with 80:20 ethyl acetate–light petroleum ether a 95:5 mixture of the (*1′RS,2′E,3SR,4RS*) and (*1′RS,2′E,3RS,4SR*) diastereomers **53** and **54** of *3-(1,1-dimethylethoxy)-4-[3′-(diphenylphosphinoyl)-1′-pentylprop-2′-enyl]cyclopentanone* as a colorless oil (875 mg, 81%): IR ($CHCl_3$) ν_{max} 2970 (s), 1740 (s), 1630 (w), 1440 (w), 1370 (m), 1180 (s), 1120 (m), 1100 (m), 1000 (w) cm^{-1}; ^1H NMR (major isomer) δ 0.85 (3 H, t, J = 7.5 Hz, CH_3), 1.13 (9 H, s, *t*-Bu), 1.16–1.57 (8 H, m), 1.97 (1 H, ddd, J = 18.0, 9.5, 1 Hz, H5β), 2.15 (1 H, ddd, J = 18.5, 6.3, 1.2 Hz, H2α), 2.25 (1 H, dddd, J = 9.5, 8.3, 6.8, 6.2 Hz, H4α), 2.41 (1 H, m, H1′), 2.42 (1 H, ddd, J = 18.0, 8.3, 1.5 Hz, H5α), 2.51 (1 H, ddd, J = 18.5, 6.5, 1 Hz, H2β), 4.01 (1 H, ddd, J = 6.6, 6.0, 6.2 Hz, H3β), 6.26 (1 H, ddd, J = 24.8, 16.9, 0.6 Hz, H3′), 6.62 (1 H, ddd, J = 19.0, 16.9, 9.0 Hz, H2′), 7.43–7.75 (10 H, m, C_6H_5); MS m/e 466 (M^+, 1), 409 (10), 392 (10), 339 (12), 326 (15), 325 (43), 312 (35), 311 (63), 355 (11), 203 (15), 202 (53), 201 (45). Anal. Calcd for $C_{29}H_{39}O_3P$: C, 74.7; H, 8.4; P, 6.7. Found: C, 74.3; H, 8.6; P, 6.8.

From the phosphine oxide (*Z*/*E* 83:17) (482 mg, 1.55 mmol) and the enone (264 mg, 1.70 mmol) after flash chromatography with 70:30 ethyl acetate–light petroleum was obtained an 82:18 mixture of the diastereomers **54** and **53** as a colorless oil (600 mg, 83%). Upon standing at 4 °C, the oil became a white solid, mp 80–81 °C, which could not be recrystallized: IR (neat) ν_{max} 2970 ns), 1740 (s), 1630 (s), 1440 (w), 1370 (m), 1180 (s), 1120 (m), 1100 (m), 1000 (w) cm^{-1}; ^1H NMR (major isomer) δ 0.87 (3 H, t, J = 7.5 Hz, CH_3), 1.08 (9 H, s, *t*-Bu), 1.22–1.57 (8 H, m), 1.96 (1 H, dd, J = 17.7, 10.8 Hz, H5β), 2.14 (1 H, ddd, J = 18.6, 8.1, 1.8 Hz, H2α), 2.27 (1 H, dddd, J = 9.5, 8.3, 8.1, 4.5 Hz, H4α), 2.34 (1 H, ddd, J = 17.7, 7.9, 1.8 Hz, H5α), 2.56 (1 H, dd, J = 18.6, 6.9 Hz, H2β), 2.68 (1 H, ddm, J = 9.2, 4.5 Hz, H1′), 3.87 (1 H, ddd, J = 8.1, 8.1, 7.2 Hz, H3β), 6.31 (1 H, ddd, J = 26.0, 16.9, 0.6 Hz, H3′), 6.65 (1 H, ddd, J = 19.0, 16.9, 9.2 Hz, H2′), 7.43–7.75 (10 H, m, C_6H_5); MS m/e 466 (M^+, 1), 409 (8), 392 (10), 339 (12), 326 (15), 325 (46), 312 (37), 311 (64), 225 (13), 202 (53), 201 (45), 57 (100). Anal. Calcd for $C_{29}H_{39}O_3P$: C, 74.7; H, 8.4. Found: C, 74.7; H, 8.5.

Cyclopent-2-enone with (i) But-2-enyldiphenylphosphine Oxide (15). The phosphine oxide (*E*/*Z* >99.5:0.5) (439 mg, 1.72 mmol) and the enone (161 mg, 1.96 mmol) at −70 °C gave after flash chromatography with 90:10 ethyl acetate–light petroleum a single diastereomer as a white solid. Recrystallization from ethyl acetate–light petroleum gave *(1′RS,2′E,3RS)-3-[3′-(diphenylphosphinoyl)-1′-methylprop-2′-enyl]-cyclopentanone* (**55**; 460 mg, 80%) as needles: mp 85–87 °C; IR ($CHCl_3$) ν_{max} 2950 (s), 1730 (s), 1610 (w), 1430 (m), 1390 (w), 1370 (w), 1350 (w), 1170 (s), 1120 (s), 1090 (m) cm^{-1}; ^1H NMR δ 1.13 (3 H, d, J = 6.8 Hz, CH_3), 1.48–1.62 (1 H, m, H4β), 1.88 (1 H, ddd, J = 18.3, 11.5, 1.4 Hz, H2β), 2.06–2.45 (5 H, m, H1′, H2α, H3α, H4α, H5α, H5β), 6.29 (1 H, ddd, J = 24.8, 16.8, 1.1 Hz, H3′), 6.71 (1 H, ddd, J = 19.4, 16.8, 8.0 Hz, H2′), 7.40–7.75 (10 H, m, C_6H_5); MS m/e 338 (M^+, 1), 203 (20), 202 (100), 201 (20), 183 (10), 155 (8). Anal. Calcd for $C_{21}H_{23}O_2P$: C, 74.5; H, 6.8; P, 9.2. Found: C, 74.5; H, 6.9; P, 9.5.

From the phosphine oxide (*Z*/*E* 95:5) (452 mg, 1.76 mmol) and the enone (163 mg, 1.98 mmol) after flash chromatography with 90:10 ethyl acetate–light petroleum was obtained (*1'RS,2'E,3SR*)-*3*-[*3'*-(*diphenylphosphinoyl*)-*1'*-*methylprop-2'-enyl*]*cyclopentanone* (**56**) as a colorless viscous oil (676 mg, 81%) containing 5% of the diastereomer **55**: IR (neat) ν_{max} 2960 (s), 1730 (s), 1620 (m), 1440 (s), 1400 (m), 1380 (m), 1240 (s), 1180 (s), 1040 (m), 1000 (m); ^{1}H NMR δ 1.15 (3 H, d, J = 6.8 Hz, CH_3) 1.48–1.62 (1 H, m, H4β), 1.84 (1 H, ddd, J = 18.4, 11.0, 1.3 Hz, H2β), 2.05–2.35 (5 H, m, H2α, H3α, H4α, H5α, H5β), 2.36–2.45 (1 H, m, H1'), 6.30 (1 H, ddd, J = 24.6, 16.8, 1.1 Hz, H3'), 6.68 (1 H, ddd, J = 19.4, 16.8, 8.0 Hz, H2'), 7.45–7.74 (10 H, m, C_6H_5); MS *m*/*e* 338 (M^+, 2), 256 (30), 255 (15), 203 (17), 202 (100), 201 (20), 183 (8); HRMS calcd for $C_{21}H_{23}O_2P$ 338.1435, found 338.1451.

(ii) Diethyl But-2-enylphosphonate (16). The phosphonate (*E*/*Z* 78:22) (576 mg, 3.0 mmol) and the enone (245 mg, 3.0 mmol) at −70 °C after flash chromatography with 85:15 ethyl acetate–light petroleum gave a 77:23 mixture of the (*1'RS,2'E,3RS*) and (*1'RS,2'E,3SR*) diastereomers **57** and **58** of *3*-[*3'*-(*diethylphosphonoyl*)-*1'*-*methylbut-2'-enyl*]*cyclopentanone* as a colorless oil (664 mg, 81%), bp 190–200 °C (0.5 mm; (Kugelrohr): IR (neat) ν_{max} 2980 (s), 1740 (s), 1630 (m), 1450 (w), 1400 (m), 1370 (w), 1250 (s), 1160 (s), 1020 (s), 960 (s), 840 (m), 720 (m) cm^{-1}; ^{1}H NMR (major isomer) δ 1.11 (3 H, d, J = 6.6 Hz, CH_3), 1.34 (6 H, t, J = 7.2 Hz, CH_3), 1.48–1.68 (1 H, m, H4β), 1.875 (1 H, ddd, J = 18.3, 10.8, 1.5 Hz, H2β), 2.05–2.45, 6 H, m, H2α, H3α, H4α, H5α, H5β, H1'), 4.02–4.13 (4 H, m, CH_2), 5.69 (1 H, ddd, J = 20.5, 17.2, 1.2 Hz, H3'), 6.71 (1 H, ddd, J = 22.0, 17.2, 8.25 Hz H2'); MS *m*/*e* 274 (M^+, 4), 259 (4), 246 (14), 193 (13), 192 (100), 191 (14), 178 (15), 164 (26); HRMS calcd for $C_{13}H_{23}O_4P$ 274.13348 found 274.1336.

The phosphonate (*Z*/*E* 87:13) (484 mg, 2.52 mmol) and the enone (227 mg, 2.77 mmol) after flash chromatography with 85:15 ethyl acetate–light petroleum gave a 87:13 mixture of the diastereomers **58** and **57** of the above product as a colorless oil (510 mg, 74%), bp 190–200 °C (0.5 mm; Kugelrohr): IR (neat) ν_{max} 2980 (s), 1740 (s), 1630 (m), 1460 (m), 1400 (m), 1240 (s), 1160 (m), 1030 (s), 960 (s), 830 (m) cm^{-1}; ^{1}H NMR (major isomer) δ 1.14 (3 H, d, J = 6.8 Hz, CH_3), 1.33 (6 H, t, J = 7.2 Hz, CH_3), 1.50–1.65 (1 H, m, H4β), 1.85 (1 H, ddd, J = 18.6, 11.1, 1.4 Hz, H2β), 2.07–2.36 (6 H, m, H2α, H3α, H4α, H5α, H5β, H1'), 4.02–4.13 (4 H, m, CH_2), 5.67 (1 H, ddd, J = 20.4, 17.3, 1.3 Hz, H3'), 6.68 (1 H, dddd, J = 22.0, 17.3, 8.0 Hz, H2'); MS *m*/*e* 274 (M^+, 6), 246 (13), 193 (12), 192 (100), 191 (17), 178 (20), 164 (19); HRMS calcd for $C_{13}H_{22}O_4P$ 274.1334, found 274.1332.

Cyclohex-2-enone with But-2-enyldiphenylphosphine Oxide (15). The phosphine oxide (468 mg, 1.83 mmol) with the enone (195 mg, 2.03 mmol) gave after flash chromatography with 80:20 ethyl acetate–light petroleum ether a 1:1 mixture of two diasteromers of *3*-[*1'*-*methyl-3'*-(*diphenylphosphinoyl*)*prop-2'-enyl*]*cyclohexanone* (**59**) as a colorless oil (470 mg, 73%). Similar results were obtained when the carbanion was generated at −40 °C, treated with the enone at −30 °C, and quenched at −10 °C: IR (neat) ν_{max} 2950 (s), 1710 (s), 1440 (s), 1320 (m), 1230 (m), 1190 (s), 1130 (s), 1110 (s), 1080 (w), 1000 (m), 760 (s), 740 (s), 700 (s) cm^{-1}; ^{1}H NMR δ 1.09 (3 H, d, J = 6.8 Hz, CH_3), 1.5–2.5 (9 H, m, H1', H2, H3, H4, H5, H6, H1), 6.26 (1 H, ddd, J = 24.5, 16.8, 1.1 Hz, H3'), 6.73 (1 H, ddd, J = 19.6, 7.6 Hz, H2'), 6.4–6.8 (10 H, m, C_6H_5); MS *m*/*e* 352 (M^+, 4), 257 (20), 256 (80), 255 (10), 203 (200), 202 (100), 201 (30), 183 (10), 155 (9). Anal. Calcd for $C_{22}H_{25}O_2P$: C, 75.0; H, 7.1. Found: C, 74.6; H, 7.5.

Addition of the enone (162 mg, 1.68 mmol) in THF (5 mL) containing anhydrous lithium bromide (162 mg, 1.82 mmol) to the lithiated phosphine oxide (from the phosphine oxide; 411 mg, 1.61 mmol) at −70 °C gave the product **59** (480 mg, 85%).

Cyclohept-2-enone with But-2-enyldiphenylphosphine Oxide (15). The crude product obtained from the phosphine oxide (472 mg, 1.84 mmol) and cyclohept-2-enone (233 mg, 2.03 mmol) was submitted to flash chromatography with 40:60 ethyl acetate–light petroleum ether to give first an 80:20 mixture of diastereomers of the carbonyl addition product *1*-[*1'*-(*diphenylphosphinoyl*)*but-2'-enyl*]*cycloheptan-2-en-1-ol* (**62**; 280 mg, 42%) as a crystalline solid, mp 140–146 °C; the isomers could not be separated by recrystallization or HPLC: IR ($CHCl_3$) ν_{max} 3340 (s), 2920 (s), 1440 (s), 1180 (m), 1160 (s), 1110 (s), 1090 (m), 980 (m) cm^{-1}; ^{1}H NMR (major isomer) δ 1.45 (3 H, ddd, J = 6.75, 5.2, 1.73 Hz, CH_3), 1.53–2.70 (8 H, m), 3.45 (1 H, dd, J = 10.6, 9.4 Hz, H1'), 5.08 (1 H, ddd, J = 12.1, 7.26, 5.06 Hz, H3), 5.36 (1 H, ddq, J = 15.4, 6.3, 4.5 Hz, H3), 5.53 (1 H, dddq, J = 15.5, 10.6, 5.1, 1.51 Hz, H2'), 5.61 (1 H, ddd, J = 12.1, 1.5, 1.4 Hz, H2), 7.36–7.91 (10 H, m, C_6H_5); MS *m*/*e* 366 (M^+, <1), 348 (6), 257 (25), 256 (100), 218 (18), 229 (9), 202 (29), 201 (32), 147 (10), 130 (12); MS (CI) *m*/*e* 367 (P + 1); HRMS calcd for [$C_{23}H_{26}O_2P - H_2O$] 348.1643, found 348.1648.

A mixture of diastereomers of the carbonyl and conjugate addition products **61** and **60** was eluted next as a colorless viscous oil (310 mg, 46%). This was submitted to HPLC (ethyl acetate, Whatman Partisil 10 M20 column, flow rate 13 mL min^{-1}, 700 psi) to give one diastereomer of (*E*)-*1*-[*3'*-(*diphenylphosphinoyl*)-*1'*-*methylprop-2'-enyl*]*cyclohept-2-en-1-ol* (**60**) as a colorless oil: IR (neat) ν_{max} 3358 (s), 2930 (s), 2860 (m), 1710 (m), 1640 (w), 1438 (s), 1174 (s), 1121 (m), 1101 (m), 998 (m), 750 (s), 722 (s), 695 (s) cm^{-1}; ^{1}H NMR δ 1.132 (3 H, d, J = 6.84 Hz, CH_3), 1.58–2.70 (8 H, m), 5.58 (1 H, dm, J = 12.0 Hz, H2), 5.764 (1 H, ddd, J = 12.0, 5.9, 5.9 Hz, H3), 6.31 (1 H, ddd, J = 24.6, 17.1, 1.0 Hz, H3'), 6.85 (1 H, ddd, J = 20.0, 17.1, 8.0 Hz, H2'), 7.43–7.78 (10 H, m, C_6H_5); MS *m*/*e* 367 (4), 366 (M^+, 4), 271 (30), 256 (35), 217 (20), 215 (19), 202 (100), 201 (93), 183 (14); HRMS calcd for $C_{23}H_{27}O_2P$ 366.1748, found 366.1750.

The second isomer of **61**, a colorless viscous oil, was eluted next: IR (neat) ν_{max} 3348 (s), 2930 (s), 2860 (m), 1710 (m), 1640 (w), 1442 (s), 1180 (s), 1119 (m), 1103 (m), 995 (m), 750 (s), 722 (s), 695 (s) cm^{-1}; ^{1}H NMR δ 1.118 (3 H, d, J = 6.8 Hz, CH_3), 1.55–2.70 (8 H, m), 5.535 (1 H, dm, J = 12.2 Hz, H2), 5.746 (1 H, ddd, J = 12.2, 5.4, 5.9 Hz, H3), 6.251 (1 H, ddd, J = 24.7, 17.3, 1.2 Hz, H3'), 6.84 (1 H, ddd, J = 20.0, 17.3, 7.8 Hz, H2'), 7.43–7.78 (10 H, m, C_6H_5); MS *m*/*e* 367 (4), 366 (M^+, 4), 348 (5), 271 (30), 256 (35), 217 (20), 215 (19), 202 (100), 201 (93), 183 (14); HRMS calcd for $C_{23}H_{27}O_2P$ 366.1748, found 366.1750.

The next fraction eluted was one diastereomer of (*E*)-*3*-[*3'*-(*diphenylphosphinoyl*)-*1'*-*methylprop-2'-enyl*]*cycloheptanone* (**60**), a colorless viscous oil: IR (neat) ν_{max} 2930 (s), 2860 (m), 1699 (s), 1620 (w), 1438 (s), 1184 (s), 1121 (s), 1104 (m), 1000 (m), 740 (s), 721 (s), 696 (s), 751 (s) cm^{-1}; ^{1}H NMR δ 1.085 (3 H, d, J = 6.8 Hz, CH_3), 1.25–2.50 (12 H, m), 6.23 (1 H, ddd, J = 24.4, 17.2, 1 Hz, H3'), 6.685 (1 H, ddd, J = 19.5, 17.2, 7.0 Hz, H2'), 7.38–7.74 (10 H, m, C_6H_5); MS *m*/*e* 366 (M^+, 9), 256 (95), 227 (100), 215 (12), 203 (25), 202 (100), 183 (14), 165 (13), 155 (12); HRMS calcd for $C_{23}H_{27}O_2P$ 366.1748, found 366.1750.

The most polar fraction was the second isomer of **60**: IR (neat) ν_{max} 2930 (s), 2860 (m), 1697 (s), 1620 (w), 1442 (s), 1184 (s), 1120 (s), 1103 (m), 1000 (m), 740 (s), 721 (s), 693 (s), 751 (s) cm^{-1}; ^{1}H NMR δ 1.084 (3 H, d, J = 6.8 Hz, CH_3), 1.25–2.50 (12 H, m), 6.24 (1 H, ddd, J = 24.6, 17.1, 1.1 Hz, H3'), 6.71 (1 H, ddd, J = 19.8, 17.1, 7.1 Hz, H2'), 7.38–7.74 (10 H, m, C_6H_5); MS *m*/*e* 366 (M^+, 9), 311 (7), 256 (95), 241 (9), 227 (100), 215 (12), 203 (25), 202 (100), 183 (14), 165 (13), 155 (12); HRMS calcd for $C_{23}H_{27}O_2P$ 366.1748, found 366.1750.

Registry No. (*E*)-**1**, 85250-56-2; (*Z*)-**1**, 91789-07-0; (*E*)-**4**, 56561-12-7; (*Z*)-**4**, 73925-25-4; (*E*)-**5**, 112173-35-0; (*Z*)-**5**, 114678-51-2; (*E*)-**6**, 86838-05-3; (*Z*)-**6**, 97964-94-8; (*E*)-**7**, 114678-52-3; (*Z*)-**7**, 114678-53-4; **8**, 42185-88-6; **9**, 114678-55-6; **10**, 78012-73-4; **11**, 19093-37-9; (*E*)-**12**, 114678-58-9; (*Z*)-**12**, 114678-59-0; (*E*)-**13**, 114678-61-4; (*Z*)-**13**, 114678-62-5; (*E*)-**14**, 114678-63-6; (*Z*)-**14**, 114678-64-7; (*E*)-**15**, 17668-60-9; (*Z*)-**15**, 58322-08-0; (*E*)-**16**, 26327-86-6; (*Z*)-**16**, 26327-87-7; **17**, 73448-15-4; **18**, 497-23-4; **19**, 930-30-3; **20**, 35298-48-7; **21**, 2758-18-1; **22**, 930-68-7; **23**, 1121-66-0; **24**, 826-56-2; **25**, 110770-73-5; **26**, 110716-82-0; **27**, 114678-65-8; **28**, 114718-08-0; **29**, 114718-09-1; **30**, 114718-11-5; **31**, 114718-12-6; (*1'RS,2'E,3RS,S*$_S$*R*$_S$)-**32**, 114678-67-0; (*1'RS,2'E,3SR,R*$_S$*S*$_S$)-**32**, 114718-13-7; **33**, 114678-68-1; **34**, 114718-14-8; **35**, 114678-69-2; **36**, 114718-15-9; **37**, 114718-16-0; (*1'RS,2'E,3RS,R*$_S$*S*$_S$)-**38**, 114678-70-5; (*1'RS,2'E,3SR,S*$_S$*R*$_S$)-**38**, 114718-17-1; (*2'E,3RS,R*$_S$*S*$_S$)-**39**, 114678-71-6; (*2'E,3RS,S*$_S$*R*$_S$)-**39**, 114678-72-7; **40**, 114678-73-8; (*1'RS,2'E,3RS,R*$_S$*S*$_S$)-**41**, 114678-74-9; (*1'RS,2'E,3SR,S*$_S$*S*$_S$)-**41**, 114718-18-2; **42**, 114691-80-4; (*2'E,4RS,S*$_S$*R*$_S$)-**43**, 114718-19-3; (*2'E,4RS,R*$_S$*S*$_S$)-**43**, 114718-20-6; (*1RS,1'RS,R*$_S$*S*$_S$)-**44**, 114678-75-0; (*1RS,1'SR,R*$_S$*S*$_S$)-**44**, 114718-21-7; (*1RS,1'RS,S*$_S$*R*$_S$)-**44**, 114718-22-8; (*1RS,1'SR,S*$_S$*R*$_S$)-**44**, 114718-23-9; **45**, 114718-24-0; **46**, 114678-76-1; (*1RS,1'RS,R*$_S$*S*$_S$)-**47**, 114678-77-2; (*1RS,1'SR,R*$_S$*S*$_S$)-**47**, 114718-25-1; (*1RS,1'RS,S*$_S$*R*$_S$)-**47**, 114718-26-2; (*1RS,1'SR,S*$_S$*R*$_S$)-**47**, 114718-27-3; (*2'E,3RS,R*$_S$*S*$_S$)-**48**, 114678-79-4; (*2'E,3RS,S*$_S$*R*$_S$)-**48**, 114678-97-6; (*1RS,1'RS,R*$_S$*S*$_S$)-**49**, 114678-78-3; (*1RS,1'SR,R*$_S$*S*$_S$)-**49**, 114718-28-4; (*1RS,1'RS,S*$_S$*R*$_S$)-**49**, 114718-29-5; (*1RS,1'SR,S*$_S$*R*$_S$)-**49**, 114718-30-8; (*1RS,2'E,S*$_S$*R*$_S$)-**50**, 114678-80-7; (*1RS,2'E,R*$_S$*S*$_S$)-**50**, 114678-81-8; (*1RS,1'RS,R*$_S$*S*$_S$)-**51**, 114678-82-9; (*1RS,1'SR,R*$_S$*S*$_S$)-**51**, 114718-31-9; (*1RS,1'RS,S*$_S$*R*$_S$)-**51**, 114718-32-0; (*1RS,1'SR,S*$_S$*R*$_S$)-**51**, 114718-33-1; **52**, 114678-83-0; **53**, 114678-84-1; **54**, 114718-34-2; **55**, 114678-85-2; **56**, 114678-86-3; **57**, 114678-87-4; **58**, 114678-88-5; (*1'RS,2'E,3RS*)-**59**, 114678-89-6; (*1'RS,2'E,3SR*)-**59**, 114678-90-9; (*1'RS,2'E,3SR*)-**60**, 114678-95-4; (*1'RS,2'E,3RS*)-**60**, 114678-96-5; (*1RS,1'SR,2'E*)-**61**, 114678-94-3; (*1RS,1'RS,2'E*)-**61**, 114678-93-2; (*1RS,1'RS,2'E*)-**62**, 114678-91-0; (*1RS,1'SR,2'E*)-**62**, 114678-92-1; **63**, 114678-66-9; **65**, 114718-10-4; (*E*)-1-(methylthio)-oct-2-ene, 91944-69-3; (*E*)-1-bromobut-2-ene, 29576-14-5; (*Z*)-1-bromobut-2-ene, 39616-19-8; (*E*)-1-(phenylthio)but-2-ene, 36195-56-9; (*Z*)-1-(phenylthio)but-2-ene, 36195-55-8; sodium 2-methylpropane-2-thiolate, 29364-29-2; lithium diphenylphosphide, 4541-02-0; (*E*)-1-(1,1-dimethylethylthio)but-2-ene, 107183-90-4; (*Z*)-1-(1,1-dimethylethyl-

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

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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

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(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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