aqueous solution of $NaHCO_3$ (15 mL) and a saturated aqueous solution of NaCl (20 mL), dried (Na_2SO_4), and concentrated to give a colorless crystalline material (47 mg), which was purified by HPLC [A, EtOAc–hexane (3:7), 3.0].

The major peak (t_R 5.6 min) gave spectroscopically pure **43** (40 mg, 87%) as a colorless crystalline material, which was recrystallized from a mixture of ethyl acetate and hexane to give colorless needles, mp 176–177.5 °C.

Acknowledgment. The present work was financially supported by Grant-in-Aid for Scientific Research from Ministry of Education (No. 554155). We wish to express our thanks to Professor Ferdinand Bohlmann of Technical University Berlin, for the generous gift of the ^1H NMR and IR spectra of 3-epizaluzanin C. We also would like to thank Professor Yoshinori Asakawa of Tokushima Bunri University for the ^1H NMR and IR spectra of zaluzanin C and zaluzanin D. We also thank Professor S. Yamaguchi for a loan of a polarimeter and their help in the measurement of optical rotation, T. Kondo and H. Ando of Instrumental Analysis Center for Chemistry, Tohoku University for the measurement of ^1H NMR and microanalyses, K. Kawamura and M. Inada of Pharmacutical Institute, Tohoku University, for the measurementof high- and low-resolution mass spectra, and Dr. H. Hagiwara of Chemical Research Institute of Non-Aqueous Solution, Tohoku University, for the measurement of high-resolution mass spectra. We are indebted to Nippon Shinyaku Co., Ltd., for the generous donation of α-santonin.

Registry No. **10**, 67667-64-5; **11**, 16838-87-2; **12**, 16838-85-0; **13**, 481-06-1; **21**, 38236-17-8; **22**, 119273-10-8; **23**, 75956-97-7; **24**, 82263-12-5; **25**, 82206-87-9; **26**, 82206-88-0; **27**, 67721-76-0; **28**, 82206-91-5; **29**, 82206-90-4; **30**, 82206-89-1; **31**, 82206-93-7; **32**, 82206-92-6; **33**, 119273-11-9; **34**, 119273-12-0; **35**, 119273-13-1; **36**, 119273-14-2; **37**, 119273-15-3; **38**, 82263-14-7; **39**, 82263-13-6; **40**, 82309-42-0; **41a**, 82206-99-3; **41b**, 82206-94-8; **41c**, 82206-98-2; **42a**, 82206-96-0; **42b**, 82206-95-9; **43**, 82206-97-1; **44**, 119273-16-4.

Kinetically Controlled, Stereoselective Formation of Vinylic Sulfones by Conjugate Addition of Lithiated 3-Alkylallylic Sulfones to Cyclic Enones

Malcolm R. Binns, Richard K. Haynes,* Andrew G. Katsifis, Paul A. Schober, and Simone C. Vonwiller

Department of Organic Chemistry, The University of Sydney, Sydney 2006, New South Wales, Australia

Received October 4, 1988

Like the corresponding lithiated sulfoxides, lithiated but-2-enyl and oct-2-enyl sulfones undergo kinetically controlled, highly diastereoselective aprotic conjugate addition to five-membered cyclic enones in tetrahydrofuran to deliver vinylic sulfones whose formation and stereochemistry are rationalized in terms of planar or near-planar lithiated reagents reacting through an extended trans-decalyl or trans-fused chair–chair transition state. In contrast to cyclopentenone, 4-*tert*-butoxycyclopent-2-enone gives mixtures of conjugate and carbonyl adducts with the lithiated sulfones at −70 °C. This is ascribed to a steric effect involving the *tert*-butoxy group at C4 of the enone destabilizing the extended transition state. Reactions with cyclohexenone are less stereoselective and are temperature dependent, with lower temperatures (−85 °C) favoring carbonyl addition to generate allylic sulfones as mixtures of diastereomers. At 0 °C rapid conjugate addition takes place to give the vinylic sulfone. The lithiated alkoxides of the carbonyl adducts rearrange to the conjugate vinylic sulfones at 0 °C at a considerably slower rate than that of direct conjugate addition of the lithiated sulfone to the cyclohexenone at 0 °C. The stereoconvergence in the rearrangement excludes an intramolecular Cope rearrangement. Overall the conjugate addition reactions are more sensitive to temperature and steric effects than are the reactions involving the lithiated allylic sulfoxides and, unlike those reactions, are sensitive to the presence of hexamethylphosphoric triamide, which induces formation of allylic sulfones.

Introduction

The structures of carbanions stabilized by an α-sulfonyl group have received considerable scrutiny from both theoretical and experimental standpoints. The impetus for this has largely been provided by the lack of racemization attending the generation and reactions of such carbanions from optically active sulfone precursors.[1,2] Although previously the subject of some controversy, it now appears on the basis of recent MO calculations,[3] NMR spectroscopic[4,5] studies, and X-ray crystallographic studies[6-9] that the structures of such carbanions are planar or near-planar. An NMR study of lithiated methyl phenyl sulfone indicates a carbanion whose hybridization is intermediate between sp^2 and sp^3. By contrast, lithiated methyl phenyl sulfoxide is demonstrated by the NMR technique to be planar. X-ray studies of crystalline complexes of lithiated phenyl alkyl sulfones with either tetramethylethylenediamine (TMEDA) or diglyme reveal that the lithium cation is in the proximity of, but closer to one of, the two oxygen atoms. There are no Li–C bonding contacts, and the C1–S bond is considerably shorter than that in the neutral sulfone. The orbital containing the pair of electrons at the carbanionic center lies in a plane bisecting the O–S–O bond angle. The carbanionic sites in

(1) Cran, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York 1965; pp 48–52. Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978; pp 45–56 and references therein. Durst, T. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3 [Sulfur, Selenium, Silicon, Boron Organometallic Compounds; Jones, D. N. Ed.], pp 184–186.

(2) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396.

(3) Bors, D. A.; Streitwieser, A. *J. Am. Chem. Soc.* **1986**, *108*, 1397 and references therein.

(4) Chassaing, G.; Marquet, A. *Tetrahedron* **1978**, *34*, 1399.

(5) Chassaing, G.; Marquet, A.; Corset, J.; Froment, F. *J. Organomet. Chem.* **1982**, *232*, 293.

(6) Boche, G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 573 and references therein.

(7) Gais, H.-J.; Lindner, H. J.; Vollhardt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 859.

(8) Gais, H.-J.; Vollhardt, J.; Hellmann, G.; Paulus, H.; Lindner, H. J. *Tetrahedron Lett.* **1988**, *29*, 1259.

(9) Gais, H.-J.; Vollhardt, J.; Lindner, H. J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 938.

0022-3263/89/1954-1960$01.50/0

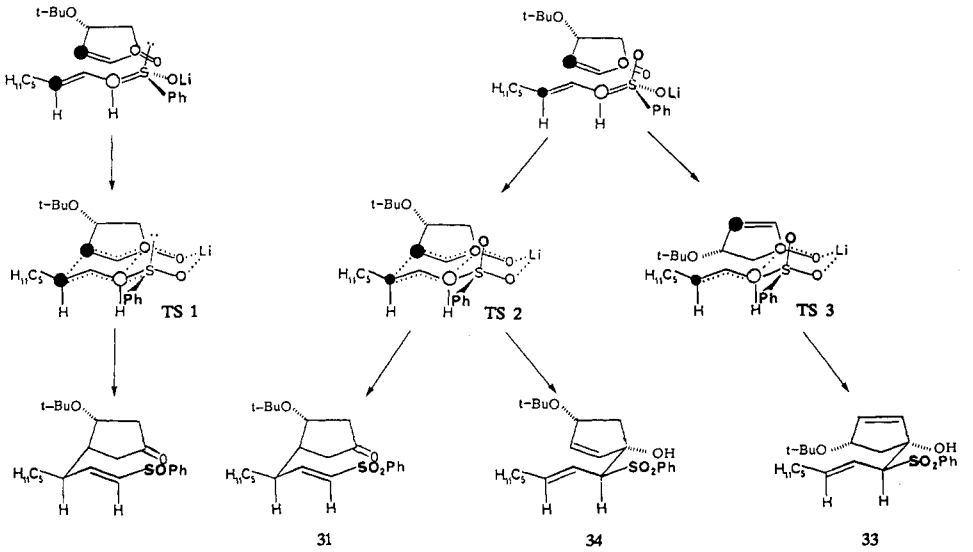


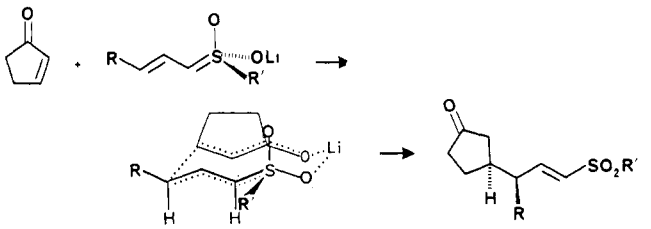
Figure 1. Transition-state representations of reactions of lithiated (*E*)-octenyl phenyl sulfoxide and lithiated (*E*)-octenyl phenyl sulfone 8 with 4-*tert*-butoxycyclopentenone (**12**) illustrating frontier orbital effects.

the lithiated methyl and benzyl phenyl sulfoxide–TMEDA complexes are near-planar and planar, respectively.[6,7] The lithiated allyl phenyl sulfone–diglyme complex has a partially pyramidal configuration at C1 corresponding to hybridization between sp^2 and sp^3.[9] As the carbanionic center is conjugated with the double bond in the allyl system, the partially pyramidal configuration at C1 as compared to the more planar configuration of the alkyl counterparts is unexpected. The lack of lithium–carbon bonding contacts is significant. The double bond character of the C1–S bond and the unsymmetrical disposition of the lithium cation with respect to the carbanionic center would seem to be sufficient in accounting for the stereoselectivity attending the reactions of lithiated allylic sulfones in general, even in those cases where the carbanionic center happens to be planar.

Lithiated (*E*)- and (*Z*)-3-alkylallylic sulfoxides undergo highly diastereoselective conjugate addition reactions with cyclic enones to deliver syn- and anti-vinylic sulfoxides arising from reaction through C3 (C_γ).[10-12] The stereo- and regiochemical outcome of the reactions are rationalized in terms of planar lithiated carbanions and trans-decalyl or trans-fused chair–chair transition state with the enone. The carbanion lies over one face of the enone in an endo orientation, with lithium associated with the oxygen atoms of the sulfoxide and the enone; the nonallylic substituent of the sulfoxide is pseudoequatorial, and the lone pair is pseudoaxial (see Figure 1). The carbanion is constrained to react through C3. A lithiated allylic sulfone clearly should be *capable* of utilizing such a transition state. If the sulfone bears an alkyl group at C3, diastereoselection will then operate in the reactions, as illustrated in Scheme I.

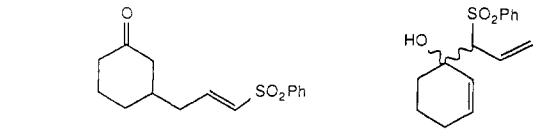
It has already been reported that lithiated allyl phenyl sulfone undergoes conjugate addition to cyclohexenone at 0 °C to give the vinylic sulfone **1**.[13] As the reaction proceeds at −78 °C to generate diastereomers of the alkoxide of the carbonyl adduct **2**, which on warming to 0 °C rearrange to the enolate of the conjugate adduct **1**, it was inferred that the formation of **1** at 0 °C proceeds under thermodynamic control.[14] The rearrangement was considered to occur in intramolecular fashion. With cyclopentenone, conjugate addition proceeds at −78 °C, although the vinylic sulfone **3** ootained from the reaction was also presumed to arise via rearrangement of a carbonyl adduct.[15] By contrast, the vinylic sulfoxides described above do not arise from the lithiated allylic sulfoxides through carbonyl intermediates; a direct, kinetically controlled conjugate addition of the lithiated allylic sulfoxides takes place.[10-12] Thus the vinylic sulfones **1** and **3** from the lithiated allyl phenyl sulfone are likely to arise in the same *kinetic* fashion as do the vinylic sulfoxides, and, moreover, the reactions would logically involve an extended transition state related to those of the sulfoxides. In the presence of HMPA, the lithiated sulfone undergoes conjugate addition with both enones to generate the allylic sulfones **4** and **5**,[14] a behavior reminiscent of that of lithiated allylic sulfides.[16-18] However, HMPA has no effect on the regiochemistry of reactions of lithiated allylic sulfoxides.[10-12,16,19]

Scheme I

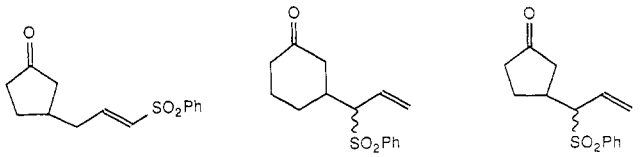


In order to verify the kinetic nature of the sulfone reactions, and to delineate more precisely those conditions that affect their regiochemical and stereochemical outcome, we have examined the reactions of the lithiated reagents derived from the 3-alkylallylic sulfones **6–10** with the enones **11–14**. The conjugate additions of the sulfoxides

(10) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, *26*, 1565. Binns, M. R.; Chai, O. L.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *Tetrahedron Lett.* **1985**, *26*, 1569.
(11) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 5411.
(12) Haynes, R. K.; Katsifis, A. G.; Vonwiller, S. C.; Hambley, T. W. *J. Am. Chem. Soc.* **1988**, *110*, 5423.
(13) Kraus, G. A.; Frazier, K. *Synth. Commun.* **1978**, *8*, 483.
(14) Hirama, M. *Tetrahedron Lett.* **1981**, *22*, 1905.
(15) Vasil'eva, L. L.; Mel'nikova, V. I.; Gainullina, E. T.; Pivnitskii, K. K. *J. Org. Chem. USSR* **1983**, *19*, 835.
(16) Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Tetrahedron Lett.* **1980**, *21*, 573.
(17) Binns, M. R.; Haynes, R. K. *J. Org. Chem.* **1981**, *46*, 3790.
(18) Binns, M. R.; Haynes, R. K. *Aust. J. Chem.* **1987**, *40*, 937.
(19) Binns, M. R.; Haynes, R. K.; Houston, T. L.; Jackson, W. R. *Aust. J. Chem.* **1981**, *34*, 2465.

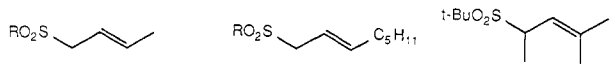


1 2

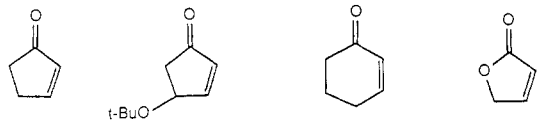


3 4 5

corresponding to the sulfones **7**–**10** have already been examined.[10-12]



6 R = *p*-Tol
7 R = Ph
8 R = Ph
9 R = Me
10



11 12 13 14

Results

The allylic sulfones **6**–**10** in tetrahydrofuran (THF) were lithiated by means of butyllithium, or lithium diisopropylamide (LDA) in the case of sulfone **6**, and then treated with the enones **11**–**14** to give the products **15**–**45** (Chart I). The reactions were usually quenched immediately after addition of the enone to the solution of the lithiated sulfone. The *E*:*Z* ratios of the starting sulfones, the conditions under which the reactions were carried out, and products with ratios and overall yields are given in Table I. The relative stereochemistries of the conjugate vinylic sulfone products were established by correlation of high-field ^{1}H NMR spectra with those of the corresponding sulfoxides.[11,12] The syn and anti-vinylic sulfones **31** and **32** were also prepared by oxidation of the sulfoxides.[10] The allylic sulfones **35** and **36** and **38** and **39** were similarly prepared from the corresponding sulfides;[18,20] relative configurations of these products have been secured by ^{1}H NMR NOE experiments.[18,20] The relative configurations of the carbonyl adducts **20**, **21**, **33**, and **34** were assigned on the basis of their high-field ^{1}H NMR spectra, as is set out in detail in the supplementary material.

As is apparent from the table, the conjugate addition reactions giving the vinylic sulfones from the five-membered enones are highly diastereoselective. Thus the 97:3 and 90:10 mixtures of the *E* and *Z* isomers of the *p*-tolyl and phenyl but-2-enyl sulfones **6** and **7** deliver the corresponding syn- and anti-vinylic sulfones **15** and **25**, and **16** and **26** with syn:anti ratios corresponding to *E*:*Z* ratios of the starting compounds. The lithiated sulfones form carbonyl adducts below −70 °C; for example, compound **17** is obtained as a mixture of diastereomers in low yield from sulfone **6** at −85 °C. Formation of carbonyl adducts does not take place with the corresponding sulfoxide, which undergoes exclusive conjugate addition at temperatures as low as −100 °C. Remarkably, the presence of a large group at C4 of the enone, as in 4-*tert*-butoxycyclopent-2-enone (**12**), partially suppresses conjugate addition in favor of a carbonyl addition through C1 to give the allylic sulfones. Thus, in addition to the conjugate adducts, the sulfones **7** and **8** with the enone **12** give the allylic carbonyl adducts **20** and **21**, and **34** and **35** at −70 °C. The presence of the large, pseudoequatorial substituent at C4 in the enone **12** ensures that H4 is pseudoaxial.[18,21] There is thus a sterically more encumbered environment about C3 than there is in cyclopentenone, which is essentially planar.[22,23] However, this steric effect is not sufficient to perturb the reactions of the lithiated sulfoxides, which undergo exclusive conjugate addition with this enone.[10-12] γ-Crotonolactone (**14**), an enone that reacts solely in conjugate fashion with stabilized carbanions,[18] provides a mixture of vinylic (compounds **37** and **40**) and allylic sulfones (compounds **38**, **39**, **41**, and **42**) in its reactions with the sulfones **8**[20] and **9**. Formation of the vinylic, but not of the allylic, sulfones is highly diastereoselective. Vinylic sulfoxides are exclusively obtained from reactions of the corresponding sulfoxides with this enone.[10-12]

Reaction of cyclohexenone with the sulfones **6** and **7** provides diastereomeric mixtures of carbonyl adducts **22** and **28** at low temperatures. However, at about 0 °C, exclusive and rapid formation (≤30 s) of the conjugate adducts **23** and **24**, and **29** and **30**, takes place. Diastereoselection is poorer than in the cyclopentenone reactions. Notably, the lithium alkoxides of a 68:32 mixture of diastereomers of the carbonyl adduct **22** did indeed rearrange at 0 °C to generate after quenching the vinylic adducts **23** and **24**. However, the ratio of these products was 89:11—the same as that obtained in the conjugate addition conducted at 0 °C (Table I). Similarly, a 75:25 mixture of diastereomers of the carbonyl adduct **28** gave an 82:18 mixture of the vinylic sulfones **29** and **30**. Further, through monitoring the progress of the rearrangement of the alkoxides from the 68:32 mixture of diastereomers of the carbonyl adduct **22** by withdrawing and quenching aliquots at time intervals, and analyzing these by ^{1}H NMR spectroscopy, it was established that the rearrangement is slower, by a factor of ≥150, than the conjugate addition of the lithiated sulfone **6** to cyclohexenone at 0 °C. In this regard, the reactions of the trimethylallyl sulfone **10** with cyclohexenone are significant. Whereas at −70 °C there was no detectable reaction, a clean reaction took place at −15 °C to generate *solely* the conjugate adduct **44**. The presence of the methyl group at C1 prevents carbonyl addition leading to an allylic sulfone from taking place. Notably, the reaction with cyclopentenone takes place at −70 °C to generate the conjugate adduct **43**.

As indicated in the table, HMPA causes the lithiated sulfones to react in conjugate fashion through C1 to deliver allylic sulfones as mixtures of diastereomers. Of particular interest here is the formation of the allylic sulfone **45** from cyclohexenone and the trimethylallyl sulfone **10** in the presence of HMPA at −70 °C. As noted above, no reaction takes place in the absence of HMPA at this temperature, although at −15 °C the vinylic sulfone **30** is formed.

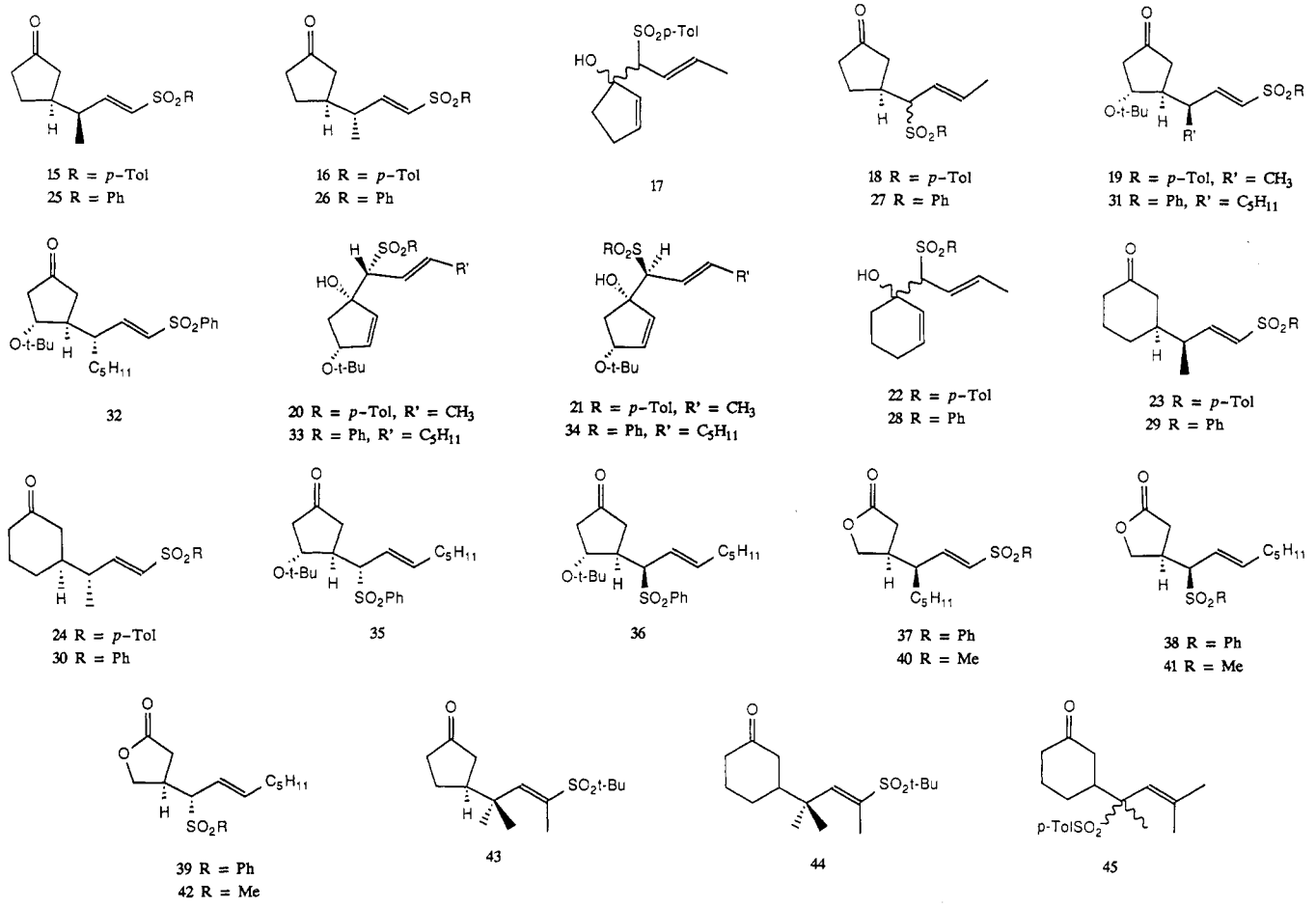
Discussion

There is obviously a close structural relationship be-

(20) Haynes, R. K.; Schober, P. A.; Binns, M. R. *Aust. J. Chem.* **1987**, *40*, 1223.

(21) Fuchs, B. *Top. Stereochem.* **1978**, *10*, 3 and references therein.
(22) Chadwick, D.; Legon, A. C.; Miller, D. J. *J. Chem. Soc., Faraday Trans. 2* **1979**, 302.
(23) Diastereomer ratios of conjugate adducts obtained from the enone **12** and a series of lithiated octenyl sulfides are different to those obtained from the planar enone **14**; this is ascribed to the presence of the *tert*-butoxy group at C4 of enone **12**.[20]

Chart I



tween the lithiated allylic sulfones and the lithiated allylic sulfoxides. The lithiated sulfones react with the same high stereoselectivity with cyclopentenones as the corresponding sulfoxides; they clearly react in a single conformation and are configurationally stable with respect to rotation about the C1–S and C2–C3 bonds. In providing vinylic sulfones whose relative stereochemistry at the allylic center is the same as that of the sulfoxides, the lithiated sulfones utilize transition states analogous to those discussed for the sulfoxides.[10-12] Thus, as depicted in Scheme I, the (*E*)-3-alkylallylic sulfones react through the trans-decalyl TS with cyclopentenone to deliver syn-vinylic sulfones. According to the model, the (*Z*)-allylic sulfones will produce anti products.

Nevertheless, reactions of the lithiated sulfones with cyclohexenone are less stereoselective than those of the sulfoxides.[11] This can be attributed in part to diaxial interactions between the pseudoaxial S–O bond of the sulfone and the cyclohexane nucleus destabilizing the normal trans-decalyl TS with respect to other extended transition states of the type discussed elsewhere. There are no such interactions in the TS of the sulfoxides. While these specific steric effects may cause the sulfones **6** and **7** to undergo carbonyl addition with cyclohexenone to give allylic sulfones at lower temperatures, it is apparent from the results of the reactions of the lithiated sulfones **6**, **8**, and **9** with the enones **12** and **14** that lithiated sulfones show less tendency in general to react at C3 through the extended TS (Scheme I) than do the sulfoxides.

If frontier orbital interactions are important here, then product ratios should relate to relative sizes of the coefficients at C1 and C3 in the HOMO of the carbanion. This is illustrated in Figure 1 for reactions involving the lithiated octenyl sulfone from **8** with 4-*tert*-butoxycyclopent-2-enone (**12**) and for comparison the lithiated octenyl sulfoxide described elsewhere.[11] The coefficient at C1 is larger, relative to that at C3, in the sulfone than in the sulfoxide, in accord with the enhanced electron-withdrawing capacity of the former group.[20,24] There will be a greater tendency for reaction to proceed through C1 of each reactant, as in TS 2, than in the case of the sulfoxide, as in TS 1. Reaction through C1 in TS 2 provides the carbonyl adduct **34**, and reaction through C3 in TS 2 provides conjugate adduct **31**. However, a second, diastereomeric carbonyl adduct **33** is also obtained; its formation can be accommodated by TS 3 where relative orientation of the reactants prevents overlap through C3 of each reactant. TS 3 now corresponds to the usual six-membered chair TS encountered in the reactions of allylic carbanions with carbonyl compounds. Because of the greater degree of orbital overlap involved in TS 2, and because of steric interactions in TS 3, TS 2 is expected to be of lower energy than TS 3. The relative amounts of products formed (**31** + **34** vs **33**, entry 14, Table I) also suggests that this is the case. The combined amounts of the corresponding adducts **19** and **21** (from the "extended" TS 2) is also greater than that of **20** ("carbonyl" TS 3) from the sulfone **6** (entry 4, Table I and the Experimental Section).

It is important to recognize the operation of a complementary effect in which carbonyl complexation by lithium affects coefficients at C1 and C3 in the enone LUMO. It has been shown that association of an enone carbonyl with

(24) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1982; pp 121–128.

Table I. Yields of Conjugate and Carbonyl Addition Products from Lithiated Allylic Sulfones

entry	sulfone	E:Z ratio	enone	T,[a] °C	products	product ratio	yield, %
1	6	97:3	11	−85, −85, −85	15, 16	96:4	76
					17	75:25[b]	5
2	6	97:3	11	−70, −3, 2	15, 16	95:5	83
3	6[c]	>99.5:0.5	11	−70, −70, −70	15		5
					18	95:5[b]	88
4	6	>99.5:0.5	12	−70, −70, −70	19		38
					20, 21	71:29	45
5	6	>99.5:0.5	12	−70, 0, 0	19		43[d]
6	6	97:3	13	−85, −85, −85	22	54:46[b]	81
7	6	97:3	13	−70, −3, 1	22	48:52[b]	5
					23, 24	93:7	69
8	7	90:10	11	−70, −70, −70	25, 26	89:11	79
9	7[e]	90:10	11	−70, −70, −70	25, 26	89:11	20
					27	94:6[b]	69
10	7	90:10	11	−70, −3, 4	25, 26	89:11	76
11	7	90:10	13	−70, −70, −70	28	75:25[b]	48
					29, 30	78:22	25
12	7	90:10	13	−70, −70, 0	29, 30	81:19	82
13	7	90:10	13	−70, −4, 2	29, 30	79:21	79
14	8	90:10	12	−70, −70, −70	31, 32	93:7	21
					33, 34	51:49	49
15	8[f]	90:10	12	−70, −70, −70	31		3.5
					33, 34		9
					35, 36	29:71	69
16	8	90:10	14	−70, −70, −70	37		8[g]
					38, 39	55:45	75[g]
17	8[e]	90:10	14	−70, −70, −70	37		3[g]
					38, 39	57:43	81[g]
18	9	>97:3	14	−70, −70, −70	40		19
					41, 42	38:62	60
19	9[e]	>97:3	14	−70, −70, −70	40		<2
					41, 42	40:60	72
20	10	–	11	−70, −70, −70	43		83
21	10	–	13	−70, −15, −15	44		72
22	10[c]	–	13	−70, −70, −70	45		61

[a] Temperature of lithiation, temperature of enone addition, temperature of quench. [b] Diastereomer ratios. [c] HMPA (3 equiv) present with lithiated sulfone. [d] Other, unidentified products also formed. [e] HMPA (1.5 equiv) present with lithiated sulfone. [f] HMPA (2 equiv) present with lithiated sulfone. [g] Data from ref 20.

Li^+ increases the coefficient at C1 relative to that at C3, thus favoring carbonyl addition.[25] Because of the lower dipole of the sulfone, Li^+ is relatively easily removed from the ion-pair situation as compared to the sulfoxide (see below). Thus, carbonyl complexation is expected to be more pronounced, or more advanced, in the TS of the sulfone reactions than in that of the sulfoxide reactions, a state of affairs that encourages carbonyl addition to occur.

Steric interactions alone are insufficient to account for the regiochemical differences between the lithiated sulfones and lithiated sulfoxides. On this basis, the sulfoxides would give the larger amount of carbonyl adduct, as there are less steric interactions apparent in TS 1 than in TS 2; as we have already seen, no carbonyl adducts are in fact obtained from the sulfoxide.

Solvation of the lithium counterion by HMPA in the lithiated allylic sulfones will also prevent access to the extended TS (cf. Scheme I); the lithiated allylic sulfones, now present as solvent separated ion pairs (ssips), will then react in a manner analogous to that discussed for the lithiated allylic sulfides[18,20] in providing the allylic sulfones. For the reactions involving cyclohexenone, the presence of ssips also assures that conjugate addition takes place.[20,29] It is significant that conjugate addition of solvent-separated lithiated allylic sulfone **10** has a lower activation energy than does the conjugate addition of the ion-paired lithiated sulfone with cyclohexenone.[30] Whereas HMPA

(25) Lefour, J.-M.; Loupy, A. *Tetrahedron* **1978**, *34*, 2597.

(26) It may also be argued that lithiated allylic sulfones are not as planar as the lithiated allylic sulfoxides, and are thus not able to utilize the extended transition states as effectively as the sulfoxides.[27] As indicated by the X-ray structure of the lithiated allyl phenyl sulfone–diglyme complex described above, C1 is nonplanar.[28] Thus, electrostatic or charge effects involving a partially pyramidal C1 and the carbonyl group may be more important in the sulfone than in the sulfoxide, thereby encouraging carbonyl addition.[25] Because of nonplanarity at C1, effective interaction at C3 is also diminished with respect to that operating in the sulfoxide. The effect is likely to apply in particular to the lithiated sulfone from **9**, which is less stabilized than that from **8**; a larger amount of allylic sulfone is formed from the latter compound in reactions involving the enone **14**.

(27) We have presented evidence in favour of planar lithiated allylic sulfoxides.[12] Unfortunately, there appears to be no X-ray data available for lithiated allylic sulfoxides. A structural comparison with lithiated allylic sulfones will be of considerable interest.

(28) As the lithiated allylic sulfone generated from **6** in the presence of diglyme in THF is more deeply colored than that either generated in THF alone, or in the presence of TMEDA in THF, we suspect that diglyme exerts a solvating effect on the lithium counterion. Also, we have found that the presence of diglyme affects the regiochemical outcome of the lithiated sulfone with cyclopentenone in providing products, as yet not fully characterized, arising by reaction through C1. TMEDA has no such effect. Thus, the X-ray data obtained from the lithiated sulfones complexed with diglyme may not necessarily be representative of the structure of lithiated sulfones in general. A comparison of O–Li bond lengths and the extent of pyramidalization at C1 in the diglyme complexes, with these parameters in the lithiated sulfones complexed with TMEDA appears worthwhile.

(29) Cohen, T.; Abraham, W. D.; Myers, M. *J. Am. Chem. Soc.* **1987**, *109*, 7923.

(30) That ssips react more rapidly with enones than do cips may be general. We have noted that inclusion of 0.2 equiv of HMPA into a solution of lithiated allyl *tert*-butyl sulfide causes formation of 38% of conjugate adduct and 62% of carbonyl adduct with cyclopentenone, whereas in its absence, carbonyl adduct only is obtained.[16] As a maximum, 20% of the carbanion is present as ssips, which thus must react more rapidly than do the contact ion pairs (cips). As the regiochemical outcome of the reactions of carbanions with enones appears to depend on the state of ion pairing,[20,29] then a consideration of the relative rates of cips and ssips of such carbanions with enones in general needs to be included in a generalized explanation of the regiochemical phenomena.

can induce formation of ssips of the lithiated sulfones, it clearly cannot do so with the lithiated sulfoxides. This effect, which must relate to the relative dipoles of the respective reagents, finds remarkable support in the results of the NMR study carried out with lithiated methyl phenyl sulfide, sulfoxide, and sulfone. The study demonstrated that whereas HMPA was able to disrupt contact ion pairs of the lithiated sulfone, it had no effect on the lithiated sulfoxide.[4] The inability of HMPA to affect the lithiated sulfoxide relates to the enhanced dipole present in the sulfoxide carbanion; this is discussed elsewhere.[11]

The disparate rates of formation of the vinylic sulfones **23** and **24**, and **29** and **30**, from the lithiated allylic sulfones **6** and **7** and cyclohexenone at 0 °C, and from rearrangement of the alkoxides of the carbonyl adducts **22** and **28**, indicate that the conjugate addition reactions proceed primarily under kinetic control. The kinetic nature of the conjugate additions are also borne out by the reactions of the sulfone **10** with cyclohexenone, where carbonyl addition does not take place. It is also apparent that the rearrangement of the alkoxides cannot proceed in an intramolecular fashion. As pointed out above, the rearrangement is stereoconvergent, and this excludes an intramolecular Cope rearrangement; the product ratio indicates that the pathway is one of dissociation–recombination.

Conclusion

The reactivity of lithiated allylic sulfones with conjugated enones is reminiscent both of that of lithiated allylic sulfoxides and of allylic sulfides. Like the sulfoxides, stereoselective kinetically controlled conjugate addition takes place to deliver vinylic products arising from reaction through C3 of the allylic system, and like the sulfides, the presence of HMPA causes kinetically controlled conjugate addition to take place to deliver allylic products arising from reaction through C1. That the regiochemical behavior of the lithiated allylic sulfone can be so precisely influenced is, in terms of the structure of the carbanion, of some interest. Clearly, lithiated allylic sulfoxides should also react with enones to give allylic sulfoxides in the presence of a reagent that induces formation of solvent separated ion pairs. The reaction of lithiated allylic sulfones bearing an alkyl group at C3 with enones to provide vinylic sulfones whose stereochemistries relate concisely to those of the starting allylic sulfone is of synthetic importance. Our further work in this area will be described elsewhere.

Experimental Section

The general experimental conditions have been described previously.[11,18,20] ^{1}H NMR spectra were recorded at 400 MHz except where otherwise indicated. 1-(Phenylsulfonyl)oct-2-ene (**8**) was prepared as described elsewhere.[20]

Preparation of Allylic Sulfones. (*E*)-1-[(4-Methylphenyl)sulfonyl]but-2-ene (6). This was prepared according to a literature method[31] to give a 69:31 mixture of the *E* and *Z* isomers of the sulfone. A solution of the product in petroleum ether was cooled to −30 °C to induce crystallization of the *E* isomer. The crystalline material so obtained was shown by NMR spectroscopy to contain less than 3% of the *Z* isomer. This was recrystallized twice more in the same fashion to give the sulfone as white needles, mp 53–55 °C, containing less than 0.5% of the *Z* isomer: ^{1}H NMR δ 1.68 (3 H, ddm, $J_{4,3}$ = 6.75, $J_{4,2}$ = 1.5 Hz, H4), 2.448 (3 H, s, CH_3), 3.71 (2 H, ddq, $J_{1,2}$ = 7.35, $J_{1,3}$ = 1.23, $J_{1,4}$ = 0.88 Hz, H1), 5.42 (1 H, dtq, $J_{2,3}$ = 14.5, $J_{2,1}$ = 7.3, $J_{2,4}$ = 1.6 Hz, H2), 5.57 (1 H, dqt, $J_{3,2}$ = 15.2, $J_{3,4}$ = 6.4, $J_{3,1}$ = 1.2 Hz, H3), 7.36–7.75 (4 H, m, ArH).

1-(Phenylsulfonyl)but-2-ene (7). 1-(Phenylthio)but-2-ene[11] (5.0 g, 30.5 mmol), containing 5–10% of the *Z* isomer, in dichloromethane (50 mL) was treated with *m*-chloroperbenzoic acid (12 g, 70 mmol) to give after the usual workup[11] a yellow oil. Purification by flash chromatography with 30:70 ethyl acetate–petroleum ether gave the sulfone[2] (5.2 g, 84%) as a colorless oil consisting of a 90:10 mixture of *E* and *Z* isomers.

(*E*)-1-(Methylsulfonyl)oct-2-ene (9). (*E*)-1-(Methylthio)-oct-2-ene[32] (*E*:*Z* > 95:5) (500 mg, 3 mmol) in dichloromethane (20 mL) at 0 °C was treated with *m*-chloroperbenzoic acid (1.6 g, 7.5 mmol) in the usual manner to give a pale yellow oil. Purification by flash chromatography with 15:85 ethyl acetate–petroleum ether gave the sulfone as a colorless liquid (520 mg, 86%) containing less than 3% of the *Z* isomer: ^{1}H NMR (100 MHz) δ 0.75–1.0 (3 H, m H8), 1.10–1.65 (6 H, m, H5–H7), 1.95–2.25 (2 H, m, H4), 2.83 (3 H, s, CH_3), 3.66 (2 H, d, $J_{1,2}$ = 6.8 Hz, H1), 5.60 (1 H, dtt, $J_{2,3}$ = 15.6, $J_{2,1}$ = 6.8, $J_{2,4}$ = 1.1 Hz, H2), 5.65 (1 H, dt, $J_{3,2}$ = 15.6, $J_{3,4}$ = 6.0 Hz, H3). Anal. Calcd for $C_9H_{18}O_2S$: C, 56.7; H, 9.5. Found: C, 56.3; H, 9.7.

4-(*tert*-Butylsulfonyl)-2-methylpent-2-ene (10). A solution of 4-(*tert*-butylthio)-2-methylpent-2-ene[12] (1.4 g, 6.9 mmol) in dichloromethane (50 mL) was treated with *m*-chloroperbenzoic acid (3.2 g, 19 mmol) to give the crude product. Recrystallization from dichloromethane–ethyl acetate gave the sulfone (1.37 g, 83%) as colorless prisms: mp 62.5–63.5 °C; ^{1}H NMR (100 MHz) δ 1.54 (3 H, d, $J_{5,4}$ = 6.9 Hz, H5), 1.50 (9 H, s, *t*-Bu), 1.84 (3 H, d, $J_{Me,3}$ = 1.5 Hz, CH_3), 1.90 (3 H, d, $J_{1,3}$ = 1.5 Hz, H1), 4.03 (1 H, dq, $J_{4,3}$ = 10.5, $J_{4,5}$ = 6.9 Hz, H2), 5.28 (1 H, dqq, $J_{3,4}$ = 10.5, $J_{3,1}$ = 1.5, $J_{3,Me}$ = 1.5 Hz, H3). Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.8; H, 9.8; S, 15.7. Found: C, 58.4; H, 9.8; S, 15.5.

Conjugate Addition Reactions. (*E*)-1-[(4-Methylphenyl)sulfonyl]but-2-ene (6) with (i) Cyclopent-2-enone. From the sulfone (*E*:*Z* 97:3) (402 mg, 1.91 mmol) in THF (30 mL) at −85 °C with butyllithium (2.1 mmol) (or LDA, 2.1 mmol), followed by the enone (173 mg, 2.1 mmol) according to the usual method at −85 °C, was obtained a pale yellow oil. Preparative layer TLC with 60:40 ethyl acetate–petroleum ether provided a 96.4:3.6 mixture of diastereomers **15** and **16** of *3-[3′-[(4-methylphenyl)sulfonyl]-1′-methylprop-2′-enyl]cyclopentanone* (425 mg, 76%): ^{1}H NMR (major isomer) δ 1.103 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 1.44–2.37 (8 H, m, H2–H5, H1′), 2.452 (3 H, s, CH_3), 6.35 (1 H, dd, $J_{3',2'}$ = 15.2, $J_{3',1'}$ = 0.96 Hz, H3′), 6.896 (1 H, dd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 8.3 Hz, H2′), 7.35–7.77 (m, ArH); (minor isomer) δ 1.131 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 1.4–2.4 (8 H, m, H2–H5, H1′), 2.432 (3 H, s, CH_3), 6.352 (1 H, dd, $J_{3',2'}$ = 15.2, $J_{3',1'}$ = 0.96 Hz, H3′), 6.901 (1 H, dd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 8.3 Hz, H2′), 7.35–7.73 (4 H, m, ArH). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.8; H, 6.9. Found: C, 66.1; H, 6.9.

A minor less polar fraction consisted of an inseparable 75:25 mixture of diastereomers of *(E)-1-[1′-[(4-methylphenyl)-sulfonyl]but-2′-enyl]cyclopent-2-en-1-ol* (**17**) (28 mg, 5%): ^{1}H NMR (major isomer) δ 1.574 (3 H, dd, $J_{4',3'}$ = 6.4, $J_{4',2'}$ = 1.9 Hz, H4′), 2.10–2.65 (4 H, m, H4, H5), 2.443 (3 H, s, CH_3), 3.807 (1 H, d, $J_{1',2'}$ = 10.3 Hz, H1′), 4.300 (1 H, s, OH), 5.17 (1 H, dq, $J_{3',2'}$ = 15.2, $J_{3',4'}$ = 6.4 Hz, H3′), 5.36 (1 H, ddq, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 10.4, $J_{2',4'}$ = 1.6 Hz, H2′), 5.75 (1 H, ddd, $J_{2,3}$ = 5.4, $J_{2,4}$ = 2.1, $J_{2,4}$ = 1.8 Hz, H2), 5.98 (1 H, ddd, $J_{3,2}$ = 5.4, $J_{3,4}$ = 2.4, $J_{3,4}$ = 1.8 Hz, H3), 7.32–7.69 (4 H, m, ArH); (minor isomer) δ 1.595 (3 H, dd, $J_{4',3'}$ = 6.4, $J_{4',2'}$ = 1.2 Hz, H4′), 1.1–2.1 (4 H, m, H4, H5), 2.434 (3 H, s, CH_3), 3.775 (1 H, d, $J_{1',2'}$ = 9.7 Hz, H1′), 4.636 (1 H, s, OH), 5.23 (1 H, dq, $J_{3',2'}$ = 16.4, $J_{3',4'}$ = 6.2 Hz, H3′), 5.32 (1 H, ddq, $J_{2',3'}$ = 16.4, $J_{2',1'}$ = 9.6, $J_{2',4'}$ = 1.2 Hz, H2′), 6.04 (1 H, ddd, $J_{2,3}$ = 5.6, $J_{2,4}$ = 2.0, $J_{2,4}$ = 1.8 Hz, H2), 6.12 (1 H, ddd, $J_{3,2}$ = 5.6, $J_{3,4}$ = 2.1, $J_{3,4}$ = 1.9 Hz, H3), 7.32–7.68 (4 H, m, ArH); HRMS calcd for $C_{16}H_{20}O_3S$ 292.1133, found 292.1130.

The sulfone **6** (*E*:*Z* 97:3) (476 mg, 2.27 mmol) in THF at −70 °C was treated with LDA (2.33 mmol). The solution was warmed to −3 °C, treated with cyclopent-2-enone (204 mg, 2.5 mmol) in THF, and quenched within 30 s with aqueous ammonium chloride, at which time the temperature was +2 °C. A pale yellow oil was obtained, which after purification by preparative layer TLC with 60:40 ethyl acetate–petroleum ether gave a 95:5 mixture of the

(31) Kocienski, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 945.

(32) Binns, M. R.; Haynes, R. K.; Lambert, D. E.; Schober, P. A.; Turner, S. G. *Aust. J. Chem.* **1987**, *40*, 281.

conjugate adducts **15** and **16** (575 mg, 83%).

From the sulfone (*E*:*Z* > 99.5:0.5) (446 mg, 2.12 mmol) in THF containing HMPA (1.14 g, 6.4 mmol) and the enone (192 mg, 2.39 mmol) at −70 °C was obtained a colorless viscous oil, a ^{1}H NMR spectrum of which indicated a 95:5 mixture of the allylic and vinylic sulfones **18** and **15**, and other products. Chromatography as described above gave a 95:5 mixture of diastereomers of *(2'E)-3-[1'-[(4-methylphenyl)sulfonyl]but-2'-enyl]cyclopentanone* (**18**) (556 mg, 88%) as a colorless oil: ^{1}H NMR δ 1.63 (3 H, d, $J_{4',3'}$ = 5.0 Hz, H4'), 1.6–1.8, 2.05–2.4, 2.53–2.62, 2.84–2.95 (6 H, m, H2-H5), 2.45 (3 H, s, CH_3), 3.47 (1 H, dd, $J_{1',2'}$ = 9.25, $J_{1',3}$ = 7.0 Hz, H1'), 5.28–5.44 (2 H, m, H2', H3'), 7.28–7.77 (4 H, m, ArH); HRMS calcd for $C_{16}H_{20}O_3S$ 292.1133, found 292.1147.

(ii) 4-*tert*-Butoxycyclopent-2-enone. From the sulfone **6** (*E*:*Z* > 99.5:0.5) (336 mg, 1.6 mmol) and the enone (270 mg, 1.76 mmol) at −70 °C was obtained a colorless viscous oil. Flash chromatography with 1:1 ether–petroleum ether gave firstly *(1RS,1'RS,2'E,4SR)-4-tert-butoxy-1-[1'-[(4-methylphenyl)-sulfonyl]but-2'-enyl]cyclopent-2-enol* (**21**) (73 mg, 13%) as fine needles: mp 110–111 °C; ^{1}H NMR δ 1.173 (9 H, s, *t*-Bu), 1.636 (3 H, dd, $J_{4',3'}$ = 6.0, $J_{4',2'}$ = 1 Hz, H4'), 1.843 (1 H, dd, $J_{5\alpha,5\beta}$ = 13.8, $J_{5\alpha,4\beta}$ = 5.3 Hz, H5α), 2.443 (3 H, s, CH_3), 2.498 (1 H, dd, $J_{5\beta,5\alpha}$ = 13.8, $J_{5\beta,4\beta}$ = 7.0 Hz, H5β), 3.708 (1 H, d, $J_{1',2'}$ = 9.5 Hz, H1'), 4.327 (1 H, dddd, $J_{4\beta,5\beta}$ = 7.0, $J_{4\beta,5\alpha}$ = 5.3, $J_{4\beta,2}$ = 1.8, $J_{4\beta,3}$ = 1.8 Hz, H4β), 4.498 (1 H, s, $W_{h/2}$ = 4 Hz, OH), 5.21–5.36 (2 H, m, H2', H3'), 5.914 (1 H, dd, $J_{3,2}$ = 5.5, $J_{3,4\beta}$ = 1.8 Hz, H3), 6.203 (1 H, dd, $J_{2,3}$ = 5.6, $J_{2,4\beta}$ = 1.6 Hz, H2), 7.29–7.69 (4 H, m, ArH). Anal. Calcd for $C_{20}H_{28}O_4S$: C, 65.9; H, 7.7. Found: C, 66.1; H, 7.4.

The second fraction was *(1RS,1'SR,2'E,4SR)-4-tert-butoxy-1-[1'-[(4-methylphenyl)sulfonyl]but-2'-enyl]cyclopent-2-enol* (**20**) (184 mg, 32%), a colorless oil: ^{1}H NMR δ 1.217 (9 H, s, *t*-Bu), 1.58 (3 H, dd, $J_{4',3'}$ = 6.3, $J_{4',2'}$ = 1.5 Hz, H4'), 1.905 (1 H, dd, $J_{5\alpha,5\beta}$ = 14.5, $J_{5\alpha,4\beta}$ = 3.8 Hz, H5α), 2.44 (3 H, s, CH_3), 2.888 (1 H, dd, $J_{5\beta,5\alpha}$ = 14.5, $J_{5\beta,4\beta}$ = 7.2 Hz, H5β), 3.664 (1 H, d, $J_{1',2'}$ = 9.8 Hz, H1'), 4.08 (1 H, s, $W_{h/2}$ = 7 Hz, OH), 4.527 (1 H, dddd, $J_{4\beta,5\beta}$ = 7.0, $J_{4\beta,5\alpha}$ = 3.5, $J_{4\beta,3}$ = 2.0, $J_{4\beta,2}$ = 1.5 Hz, H4β), 5.185 (1 H, dd, $J_{3',2'}$ = 15.2, $J_{3',4'}$ = 6.4 Hz, H3'), 5.323 (1 H, ddd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 10.0, $J_{2',4'}$ = 1.5 Hz, H2'), 5.85 (1 H, dd, $J_{3,2}$ = 5.4, $J_{3,4\beta}$ = 2.1 Hz, H3), 5.952 (1 H, dd, $J_{2,3}$ = 5.5, $J_{2,4\beta}$ = 1.2 Hz, H2), 7.29–7.70 (5 H, m, ArH). Anal. Calcd for $C_{20}H_{28}O_4S$: C, 65.9; H, 7.7. Found: C, 66.2; H, 7.9.

The third fraction was *(1'RS,2'E,3SR,4RS)-3-tert-butoxy-4-[1'-methyl-3'-[(4-methylphenyl)sulfonyl]prop-2'-enyl]cyclopentanone* (**19**) (222 mg, 38%): ^{1}H NMR δ 1.053 (3 H, d, $J_{Me,1'}$ = 7.0 Hz, CH_3), 1.182 (9 H, s, *t*-Bu), 1.888 (1 H, ddd, $J_{5\beta,5\alpha}$ = 17.5, $J_{5\beta,4\alpha}$ = 10.3 Hz, $J_{5\beta,2\alpha} \simeq$ 1 Hz, H5β), 2.196 (1 H, ddd, $J_{2\alpha,2\beta}$ = 18.1, $J_{2\alpha,3\beta}$ = 7.8, $J_{2\alpha,5\alpha}$ = 2.0 Hz, H2α), 2.234 (1 H, dddd, $J_{4\alpha,5\beta}$ = 10.0, $J_{4\alpha,5\alpha}$ = 10.0, $J_{4\alpha,3\beta}$ = 7.5, $J_{4\alpha,1'}$ = 5.3 Hz, H4α), 2.319 (1 H, ddd, $J_{5\alpha,5\beta}$ = 17.8, $J_{5\alpha,4\alpha}$ = 9.8, $J_{5\alpha,2\alpha}$ = 1.8 Hz, H5α), 2.443 (3 H, s, CH_3), 2.594 (1 H, ddd, $J_{2\beta,2\alpha}$ = 17.9, $J_{2\beta,3\beta}$ = 6.8, $J_{2\beta,5\beta}$ = 1.3 Hz, H2β), 2.659 (1 H, qddd, $J_{1',Me}$ = 7.0, $J_{1',2'}$ = 7.0, $J_{1',4}$ = 5.3, $J_{1',3'}$ = 1.4 Hz, H1'), 3.956 (1 H, ddd, $J_{3\beta,2}\alpha$ = 7.2, $J_{3\beta,2\beta}$ = 7.2, $J_{3\beta,2\alpha}$ = 7.2 Hz, H3β), 6.309 (1 H, dd, $J_{3',2'}$ = 15.3, $J_{3',1'}$ = 1.4 Hz, H3'), 6.994 (1 H, dd, $J_{2',3'}$ = 15.3 Hz, $J_{2',1'}$ = 7.1 Hz, H2'), 7.32–7.77 (4 H, m, ArH). Anal. Calcd for $C_{20}H_{28}O_4S$: C, 65.9; H, 7.7. Found: C, 65.9; H, 7.8.

Treatment of the lithiated carbanion from the sulfone (236 mg, 1.12 mmol) at 0 °C with the enone (191 mg, 1.24 mmol) gave the vinylic sulfone **19** (175 mg, 43%).

(iii) Cyclohex-2-enone. The sulfone (*E*:*Z* 97:3) (402 mg, 1.91 mmol) in THF (30 mL) under nitrogen at −85 °C was treated with LDA (2.09 mmol) followed by cyclohex-2-enone (190 mg, 1.98 mmol). The reaction mixture was then quenched after 30 s with aqueous ammonium chloride at −85 °C to give after preparative layer TLC with 60:40 ethyl acetate–petroleum ether a 54:46 mixture of diastereomers of *(E)-1-[1'-[(4-methylphenyl)-sulfonyl]but-2'-enyl]cyclohex-2-en-1-ol* (**22**) (472 mg, 81%) as a colorless oil. The oil slowly deposited a crystalline 68:32 mixture of the diastereomers, as prisms: mp 95–99 °C; ^{1}H NMR (major isomer) δ 1.575 (3 H, dd, $J_{4',3'}$ = 6.5, $J_{4',2'}$ = 1.7 Hz, H4'), 1.6–2.3 (6 H, m, H4–H6), 2.441 (3 H, s, CH_3), 3.669 (1 H, d, $J_{1',2'}$ = 10.4 Hz, H1'), 4.295 (1 H, s, OH), 5.09 (1 H, dq, $J_{3',2'}$ = 15.3, $J_{3',4'}$ = 6.5 Hz, H3'), 5.34 (1 H, ddq, $J_{2',3'}$ = 15.3, $J_{2',1'}$ = 10.4, $J_{2',4'}$ = 1.7 Hz, H2'), 5.47 (1 H, dm, $J_{2,3}$ = 10.2 Hz, H2), 5.86 (1 H, ddd, $J_{3,2}$ = 10.2, $J_{3,4}$ = 4.5, $J_{3,4}$ = 3.0 Hz, H3), 7.31–7.68 (4 H, m, ArH); (minor isomer) δ 1.584 (3 H, dd, $J_{4',3'}$ = 6.5, $J_{4',2'}$ = 1.7 Hz, H4'), 1.6–2.3 (6 H, m, H4–H6), 2.345 (3 H, s, CH_3), 3.345 (1 H, d, $J_{1',2'}$ = 10.4 Hz, H1'), 4.366 (1 H, s, OH), 5.134 (1 H, dq, $J_{3',2'}$ = 15.3, $J_{3',4'}$ = 6.5, $J_{3',1'}$ = 0.5 Hz, H3'), 5.40 (1 H, ddq, $J_{2',3'}$ = 15.3, $J_{2',1'}$ = 10.4, $J_{2',4'}$ = 1.7 Hz, H2'), 5.97 (1 H, ddd, $J_{3,2}$ = 10.2, $J_{3,4}$ = 4.5, $J_{3,4}$ = 3.0 Hz, H3), 6.15 (1 H, dm, $J_{2,3}$ = 10.2 Hz, H2), 7.31–7.68 (4 H, m, ArH). Anal. Calcd for $C_{17}H_{22}O_3S$: C, 66.7; H, 7.2. Found: C, 67.0; H, 7.5.

The sulfone (*E*:*Z* 97:3) (311 mg, 1.48 mmol) was deprotonated at −70 °C with LDA (1.62 mmol), and the solution was warmed to −3 °C and treated with the enone (155 mg, 1.61 mmol). The reaction mixture was quenched within 30 s at which time the reaction temperature was 1 °C. The pale yellow oil obtained after workup was submitted to preparative layer TLC with 60:40 ethyl acetate–petroleum ether to give starting sulfone (10%), a 48:52 mixture of diastereomers of the carbonyl adduct **22** (22.6 mg, 5%), and then an 89:11 mixture of the diastereomers **23** and **24** of *3-[3'-[(4-methylphenyl)sulfonyl]-1'-methylprop-2'-enyl]cyclohexanone* (310 mg, 69%): ^{1}H NMR (major isomer) δ 1.060 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 1.25–2.40 (10 H, m, H2–H6, H1'), 2.436 (3 H, s, CH_3), 6.32 (1 H, dd, $J_{3',2'}$ = 15.1, $J_{3',1'}$ = 0.96 Hz, H3'), 6.853 (1 H, dd, $J_{2',3'}$ = 15.1, $J_{2',1'}$ = 8.3 Hz, H2'), 7.34–7.75 (4 H, m, ArH); ^{1}H NMR (minor isomer) δ 1.064 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 1.25–2.40 (10 H, m, H2–H6, H1'), 2.412 (3 H, s, CH_3), 6.325 (1 H, m, H3'), 6.862 (1 H, dd, $J_{2',3'}$ = 15.1, $J_{2',1'}$ = 8.3 Hz, H2'), 7.34–7.73 (4 H, m, ArH); HRMS calcd for $C_{17}H_{22}O_3S$ 306.1289, found 306.1282.

1-(Phenylsulfonyl)but-2-ene (7) with (i) Cyclopent-2-enone. The sulfone (*E*:*Z* 81:19) (304 mg, 1.55 mmol) in THF (30 mL) at −70 °C under nitrogen was treated with butyllithium (1.31 mL, 1.3 M, 1.71 mol) followed by cyclopent-2-enone (140 mg, 1.71 mmol) to give a pale yellow oil. The crude product was subjected to radial chromatography with 40:60 ethyl acetate–petroleum ether to give the unreacted starting compound (65 mg) and then an inseparable 81:19 mixture of the diastereomers **25** and **26** (268 mg, 79%) of *3-[1'-methyl-3'-(phenylsulfonyl)prop-2'-enyl]-cyclopentanone* as white prisms, mp 99–101.5 °C, from ethyl acetate–petroleum ether: ^{1}H NMR (major isomer **25**) δ 1.114 (3 H, d, $J_{Me,1'}$ = 6.72 Hz, CH_3), 1.44–1.56 (1 H, m, H4β), 1.85 (1 H, ddd, $J_{2\beta,2\alpha}$ = 18.3, $J_{2\beta,3}$ = 10.75, $J_{2\beta,5\beta}$ = 1.25 Hz, H2β), 2.05–2.45 (6 H, m, H2α, H3, H4α, H5, H1'), 6.36 (1 H, dd, $J_{3',2'}$ = 15.2, $J_{3',1'}$ = 1.1 Hz, H3'), 6.94 (1 H, dd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 8.5 Hz, H2'), 7.50–7.85 (5 H, m, C_6H_5); (minor isomer **26**) δ 1.143 (3 H, d, $J_{Me,1'}$ = 6.68 Hz, CH_3), 1.4–1.6 (1 H, m, H4β), 6.34 (1 H, dd, $J_{3',2'}$ = 15.2, $J_{3',1'}$ = 1.1 Hz, H3'), 6.90 (1 H, dd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 8.5 Hz, H2'). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.8; H, 6.5. Found: C, 65.1; H, 6.6.

The sulfone **7** (*E*:*Z* 81:19) (689 mg, 3.52 mmol) in THF (30 mL) at −70 °C containing HMPA (690 mg, 3.8 mmol) was treated with butyllithium (1.95 mL, 2.0 M, 3.87 mmol) and then with cyclopent-2-enone (320 mg, 3.9 mmol) to give a yellow oil. This was submitted to radial chromatography to give firstly *3-[1-(phenylsulfonyl)but-2'-enyl]cyclopentanone* (**27**) (605 mg, 69%) as a 95:5 mixture of diastereomers: ^{1}H NMR δ (major isomer) 1.60 (3H, dd, $J_{4',3'}$ = 6.1, $J_{4',2'}$ = 1.1 Hz, H4'), 1.64–1.76 (1 H, m, H4β), 2.05–2.65 (5 H, m, H2, H4α, H5), 2.86–3.10 (1 H, m, H3), 3.52 (1 H, dd, $J_{1',2'}$ = 9.4, $J_{1',3\alpha}$ = 7.0 Hz, H1'), 5.31 (1 H, dq, $J_{3',2'}$ = 15.5, $J_{3',4'}$ = 6.1 Hz, H3'), 5.40 (1 H, ddq, $J_{2',3'}$ = 15.4, $J_{2',1'}$ = 9.3, $J_{2',4'}$ = 1.2 Hz, H2'), 7.50–7.83 (5 H, m, C_6H_5). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 64.8; H, 6.5. Found: C, 64.8; H, 6.8.

The next fraction eluted was an 89:11 mixture (168 mg, 20%) of the vinylic sulfone diastereomers **25** and **26**. A small amount of unidentified material was also isolated.

The lithiated sulfone, from the sulfone (561 mg, 2.86 mmol) and butyllithium (1.3 mL, 2.5 M, 3.02 mmol), in THF at −3 °C was treated with the enone (302 mg, 3.15 mmol). The solution was quenched after 30 s with aqueous ammonium chloride, when the temperature was 4 °C, to give after the usual workup and chromatography as described above an 89:11 mixture of the vinylic sulfones **25** and **26** (603 mg, 76%).

(ii) Cyclohex-2-enone. From the sulfone (*E*:*Z* 90:10) (738 mg, 3.77 mmol) in THF (30 mL), butyllithium (2.1 mL, 2.0 M, 4.20 mmol), and the enone (397 mg, 4.14 mmol) at −70 °C was obtained a yellow oil, which was submitted to radial chromatography with 70:30 ethyl acetate–petroleum ether. The first fraction, a pale yellow oil, was a mixture of carbonyl adducts and starting sulfone

(*E*:*Z* 90:10). The carbonyl adduct was separated from unchanged sulfone by crystallization from ethyl acetate–petroleum ether. A 75:25 mixture of diastereomers of *1-[1′-(phenylsulfonyl)but-2′-enyl]cyclohex-2-en-1-ol* (**28**) was thereby obtained as white prisms: mp 97–99 °C (313 mg, 48%); ^{1}H NMR δ (major isomer) 1.564 (3 H, dd, $J_{4',3'}$ = 6.4, $J_{4',2'}$ = 1.7 Hz, H4′), 1.65–2.32 (6 H, m. H4–H6), 3.688 (1 H, d, $J_{1',2'}$ = 10.5 Hz, H1′), 4.22 (1 H, s, OH), 5.06 (1 H, dqd, $J_{3',2'}$ = 15.3, $J_{3',4'}$ = 6.5, $J_{3',1'}$ = 0.5 Hz, H3′), 5.35 (1 H, ddq, $J_{2',3'}$ = 15.3, $J_{2',1'}$ = 10.4, $J_{2',4'}$ = 1.7 Hz, H2′), 5.49 (1 H, dm, $J_{2,3}$ = 10.1 Hz, H2), 5.88 (1 H, dddd, $J_{3,2}$ = 10.1, $J_{3,4}$ = 5.1, $J_{3,4}$ = 2.5, J = 0.6 Hz, H3), 7.52–7.86 (5 H, m, C_6H_5); (minor isomer) 1.571 (3 H, dd, $J_{4',3'}$ = 6.6, $J_{4',2'}$ = 1.7 Hz, H4′), 3.616 (1 H, d, $J_{1',2'}$ = 10.8 Hz, H1′), 4.26 (1 H, s, OH), 5.11 (1 H, dqd, $J_{3',2'}$ = 15.3, $J_{3',4'}$ = 6.5, $J_{3',1'}$ = 0.5 Hz, H3′), 5.43 (1 H, ddq, $J_{2',3'}$ = 15.3, $J_{2',1'}$ = 10.4, $J_{2',4'}$ = 1.7 Hz, H2′), 5.986 (1 H, dddd, $J_{3,2}$ = 10.3, $J_{3,4}$ = 4.8, $J_{3,4}$ = 2.8, J = 0.5 Hz, H3), 6.138 (1 H, dm, $J_{2,3}$ = 10.2 Hz, H2). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 65.8; H, 6.9. Found: C, 66.1; H, 7.0.

The second fraction (99 mg) was a mixture of unidentified compounds. The third fraction, a colorless oil, was a 78:22 mixture of diastereomers **29** and **30** of *3-[1′-methyl-3′-(phenylsulfonyl)-prop-2′-enyl]cyclohexanone* (163 mg, 25%): ^{1}H NMR (major isomer) δ 1.063 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 1.20–2.43 (10 H, m), 6.323 (1 H, dd, $J_{3',2'}$ = 14.9, $J_{3',1'}$ = 1.2 Hz, H3′), 6.891 (1 H, dd, $J_{2',3'}$ = 14.9, $J_{2',1'}$ = 8.5, Hz, H2′), 7.47–7.90 (5 H, m, C_6H_5); (minor isomer) δ 1.067 (3 H, d, $J_{Me,1'}$ = 6.8 Hz, CH_3), 6.326 (1 H, dd, $J_{3',2'}$ = 15.1, $J_{3',1'}$ = 1.2 Hz, H3′), 6.902 (1 H, dd, $J_{2',3'}$ = 15.1, $J_{2',1'}$ = 8.1, Hz, H2′); HRMS calcd for $C_{16}H_{20}O_3S$ 292.1133, found 292.1127.

The sulfone (*E*:*Z* 90:10) (756 mg, 3.86 mmol) in THF (30 mL) at −70 °C was treated with butyllithium (2.1 mL, 2.0 M, 4.24 mmol) and then the enone (410 mg, 4.27 mmol) in THF (5 mL). The solution was warmed to 0 °C, whereupon it was stirred for 1 h and then quenched with aqueous ammonium chloride. The usual workup gave a yellow oil, which after chromatographic purification gave an 81:19 mixture of the vinylic conjugate adducts **29** and **30** (889 mg, 79%).

The lithiated sulfone, prepared from the sulfone (*E*:*Z* 90:10) (539 mg, 2.75 mmol) and butyllithium (1.3 mL, 2.5 M, 3.02 mmol), in THF was treated with the enone (299 mg, 3.02 mmol) at −4 °C. The mixture was quenched after 30 s with aqueous ammonium chloride, when the temperature was +2 °C, to give a 79:21 mixture of the conjugate adducts **29** and **30** (634 mg, 79%).

1-(Phenylsulfonyl)oct-2-ene (8) with 4-*tert*-Butoxycyclopent-2-enone. From the sulfone (*E*:*Z* 90:10) (0.88 g, 3.5 mmol) and the enone (0.54 g, 3.5 mmol) at −70 °C was obtained a light yellow oil (0.99 g, 70%). Flash chromatography with 6:94 ethyl acetate–benzene and then HPLC with 17:83 ethyl acetate–petroleum ether gave firstly *(1′RS,2′E,3RS,4SR)-3-tert-butoxy-4-[1′-pentyl-3′-(phenylsulfonyl)prop-2′-enyl]cyclopentanone* (**32**) (19.8 mg, 1.4%): ^{1}H NMR δ 0.81–0.88 (3 H, m, H5″), 1.11 (9 H, s, *t*-Bu), 1.13–1.31 (6 H, m, H2″–H4″), 1.31–1.46 (1 H, m, H1″), 1.46–1.58 (1 H, m, H1″), 1.89 (1 H, dd, $J_{5\beta,5\alpha}$ = 17.4, $J_{5\beta,4\alpha}$ = 11.4 Hz, H5β), 2.16 (1 H, ddd, $J_{2\alpha,2\beta}$ = 18.6, $J_{2\alpha,3\beta}$ = 8.1, $J_{2\alpha,5\alpha} \simeq$ 1 Hz, H2α), 2.13–2.32 (1 H, m, H4α), 2.36 (1 H, ddd, $J_{5\alpha,5\beta}$ = 17.4, $J_{5\alpha,4\alpha}$ = 8.4, $J_{5\alpha,2\alpha} \simeq$ 1 Hz, H5α), 2.58 (1 H, dd, $J_{2\beta,2\alpha}$ = 18.6, $J_{2\beta,3\beta}$ = 7.2 Hz, H2β), 6.36 (1 H, d, $J_{3',2'}$ = 15.0 Hz, H3′), 6.82 (1 H, dd, $J_{2',3'}$ = 15.0, $J_{2',1'}$ = 10.0 Hz, H2′), 7.53–7.92 (5 H, m, ArH). Anal. Calcd for $C_{23}H_{34}O_4S$: C, 67.95; H, 8.4. Found: C, 68.0; H, 8.5.

The second fraction was *(1′RS,2′E,3SR,4RS)-3-tert-butoxy-4-[1′-pentyl-3′-(phenylsulfonyl)prop-2′-enyl]cyclopentanone* (**31**) (177 mg, 20%): ^{1}H NMR δ 0.75–0.85 (3 H, m, H5″), 1.00–1.27 (6 H, m, H2″–H4″), 1.17 (9 H, s, *t*-Bu), 1.27–1.40 (1 H, m, H1″), 1.45–1.60 (1 H, m, H1″), 1.93 (1 H, dd, $J_{5\beta,5\alpha}$ = 18.3, $J_{5\beta,4\alpha}$ = 9.9 Hz, H5β), 2.17 (1 H, ddd, $J_{2\alpha,2\beta}$ = 18.3, $J_{2\alpha,3\beta}$ = 7.2, $J_{2\alpha,5\alpha} \simeq$ 1 Hz, H2α), 2.21 (1 H, dddd, $J_{4\alpha,5\beta}$ = 9.9, $J_{4\alpha,5\alpha}$ = 8.1, $J_{4\alpha,3\beta}$ = 7.0, $J_{4\alpha,1'}$ = 6.6 Hz, H4α), 2.33 (1 H, dddd, $J_{1',1''}$ = 10.3, $J_{1',2'}$ = 9.5, $J_{1',4\alpha}$ = 6.6, $J_{1',1''}$ = 3.0 Hz, H1′), 2.42 (1 H, ddd, $J_{5\alpha,5\beta}$ = 18.3, $J_{5\alpha,4\alpha}$ = 8.1, $J_{5\alpha,2\alpha} \simeq$ 1 Hz, H5α), 2.54 1 H, dd, $J_{2\beta,2\alpha}$ = 18.3, $J_{2\beta,3\beta}$ = 6 Hz, H2β), 3.97 (1 H, ddd, $J_{3\beta,4}\alpha$ = 7.0, $J_{3\beta,2\alpha}$ = 7.0, $J_{3\beta,2\beta}$ = 6.6 Hz, H3β), 6.34 (1 H, d, $J_{3',2'}$ = 15.0 Hz, H3′), 6.88 (1 H, dd, $J_{2',3'}$ = 15.0, $J_{2',1'}$ = 9.5 Hz, H2′), 7.51–7.85 (5 H, m, ArH). Anal. Calcd for $C_{23}H_{34}O_4S$: C, 67.95; H, 8.43. Found: C, 67.6; H, 8.5.

The third fraction was *(1RS,1′RS,2′E,4SR)-4-tert-butoxy-1-[1′-(phenylsulfonyl)oct-2′-enyl]cyclopent-2-enol* (**34**) (346 mg, 24%): ^{1}H NMR δ 0.87 (3 H, m, H8′), 1.07–1.39 (6 H, m, H5′, H6′, H7′), 1.17 (9 H, s, *t*-Bu), 1.86 (1 H, dd, $J_{5\alpha,5\beta}$ = 13.7, $J_{4\alpha,4\beta}$ = 7.3 Hz, H5α), 1.90–1.98 (2 H, m, H4′), 2.52 (1 H, dd, $J_{5\beta,5\alpha}$ = 13.7, $J_{5\beta,4\beta}$ = 7.0 Hz, H5β), 3.76 (1 H, d, $J_{1'}{}_{,2'}$ = 9.5 Hz, H1′), 4.33 (1 H, dddd, $J_{4\beta,5\alpha}$ = 7.3, $J_{4\beta,5\beta}$ = 7.0, $J_{4\beta,3}$ = 1.7, $J_{4\beta,2}$ = 1.3 Hz, H4β), 4.52 (1 H, s, $W_{h/2}$ = 6 Hz, OH), 5.22 (1 H, dd, $J_{2',3'}$ = 15.2, $J_{2',1'}$ = 9.5 Hz, H2′), 5.28 (1 H, dt, $J_{3',2'}$ = 15.2, $J_{3',4'}$ = 6.3 Hz, H3′), 5.93 (1 H, dd, $J_{3,2}$ = 5.7, $J_{3,4\beta}$ = 1.7 Hz, H3), 6.23 (1 H, dd, $J_{2,3}$ = 5.7, $J_{2,4\beta}$ = 1.3 Hz, H2), 7.49–7.84 (5 H, m, ArH); MS *m*/*e* 406 (M^+, ≪1), 389 (<1), 350 (1), 333 (1), 252 (8), 110 (28), 81 (63), 77 (27), 69 (100), 57 (80), 55 (62), 41 (67); HRMS calcd for $C_{23}H_{34}O_4S - C_4H_8$ 350.1552, found 350.1565.

The most polar fraction was *(1RS,1′SR,2′E,4SR)-4-tert-butoxy-1-[1′-(phenylsulfonyl)oct-2′-enyl]cyclopent-2-enol* (**33**) (347 mg, 25%): ^{1}H NMR δ 0.85 (3 H, m, H8′), 1.04–1.30 (6 H, m, H5′, H6′, H7′), 1.22 (9 H, s, *t*-Bu), 1.85–1.93 (2 H, m, H4′), 1.91 (1 H, dd, $J_{5\alpha,5\beta}$ = 14.2, $J_{5\alpha,4\beta}$ = 4.0 Hz, H5α), 2.89 (1 H, dd, $J_{5\beta,5\alpha}$ = 14.2, $J_{5\beta,4\beta}$ = 7.1 Hz, H5β), 3.69 (1 H, d, $J_{1',2'}$ = 10.0 Hz, H1′), 4.00 (1 H, s, $W_{h/2}$ = 130 Hz, OH), 4.52 (1 H, ddd, $J_{4\beta,5\beta}$ = 7.1, $J_{4\beta,4\alpha}$ = 4.0, $J_{4\beta,3}$ = 2.0, $J_{4\beta,2}$ = 1.0 Hz, H4β), 5.17 (1 H, dt, $J_{3',2'}$ = 15.4, $J_{3',4'}$ = 6.8 Hz, H3′), 5.32 (1 H, dd, $J_{2',3'}$ = 15.4, $J_{2',1'}$ = 10.0 Hz, H2′), 5.85 (1 H, dd, $J_{3,2}$ = 5.6, $J_{3,4\beta}$ = 2.0 Hz, H3), 5.99 (1 H, dd, $J_{2,3}$ = 5.6, $J_{2,4\beta}$ = 1.0 Hz, H2), 7.49–7.85 (5 H, m, ArH): MS *m*/*e* 406 (M^+, <1), 289 (<1), 350 (1), 333 (1), 252 (13), 143 (20), 111 (21), 110 (35), 81 (67), 77 (26), 69 (100), 57 (90), 55 (61), 53 (33), 41 (64); HRMS calcd for $C_{23}H_{34}O_4S - C_4H_8$ 350.1552, found 350.1545.

From the sulfone (880 mg, 3.5 mmol) and the enone (540 mg, 3.5 mmol) in THF containing HMPA (1.24 mL, 7.0 mmol) at −70 °C was obtained a light yellow oil (1.25 g). The crude oil was submitted to preparative TLC with 15:85 ethyl acetate–petroleum ether and then to HPLC with 17:83 ethyl acetate–petroleum ether. The least polar fraction was *(1′RS,2′E,3RS,4RS)-3-tert-butoxy-4-[1′-(phenylsulfonyl)oct-2′-enyl]cyclopentanone* (**36**) (251 mg, 20%): ^{1}H NMR δ 0.87 (3 H, m, H8′), 1.09–1.31 (6 H, m, H5′–H7′), 1.13 (9 H, s, *t*-Bu), 1.94–2.01 (2 H, m, H4′), 2.18 (1 H, dd, $J_{5\beta,5\alpha}$ = 18.0, $J_{5\beta,4\alpha}$ = 11.9 Hz, H5β), 2.19 (1 H, ddd, $J_{2\alpha,2\beta}$ = 18.0, $J_{2\alpha,3\beta}$ = 8.0, $J_{2\alpha,5\alpha} \simeq$ 1 Hz, H2α), 2.60 (1 H, dd, $J_{2\beta,2\alpha}$ = 18.0, $J_{2\beta,3\beta}$ = 7.0 Hz, H2β), 2.71 (1 H, ddd, $J_{5\alpha,5\beta}$ = 18.0, $J_{5\alpha,4\alpha}$ = 8.4, $J_{5\alpha,2\alpha} \simeq$ 1 Hz, H5α), 2.94 (1 H, ddd, $J_{4\alpha,5\beta}$ = 11.9, $J_{4\alpha,3\beta}$ = 8.4, $J_{4\alpha,5\alpha}$ = 8.4, $J_{4\alpha,1'}$ = 3.1 Hz, H4α), 3.85 (1 H, ddd, $J_{3\beta,2\alpha}$ = 8.0, $J_{3\beta,4\alpha}$ = 8.4, $J_{3\beta,2\beta}$ = 7.0 Hz, H3β), 3.88 (1 H, dd, $J_{1'}{}_{,2'}$ = 9.2, $J_{1,3\beta}$ = 3.1 Hz, H1′), 5.36–5.45 (2 H, m, H2′, H3′), 7.49–7.87 (5 H, m, ArH). Anal. Calcd for $C_{23}H_{34}O_4S$: C, 67.95; H, 8.43. Found: C, 68.0; H, 8.5.

The second fraction was *(1′RS,2′E,3SR,4SR)-3-tert-butoxy-4-[1′-(phenylsulfonyl)oct-2′-enyl]cyclopentanone* (**35**) (700 mg, 49%): ^{1}H NMR δ 0.87 (3 H, m, H8′), 1.04–1.30 (6 H, m, H5′–H7′), 1.24 (9 H, s, *t*-Bu), 1.84–1.94 (2 H, m, H4′), 2.17 (1 H, dd, $J_{2\alpha,2\beta}$ = 18.8, $J_{2\alpha,3\beta}$ = 5.2 Hz, H2α), 251 (1 H, dd, $J_{2\beta,2\alpha}$ = 18.8, $J_{2\beta,3\beta}$ = 6.8 Hz, H2β), 2.52–2.63 (1 H, m, H5β), 2.76–2.85 (1 H, m, H5α), 2.82–2.89 (1 H, m, H4α), 3.55 (1 H, dd, $J_{1',2'}$ = 10.2, $J_{1',4\alpha}$ = 5.4 Hz, H1′), 4.60 (1 H, ddd, $J_{3\beta,2\beta}$ = 6.8, $J_{3\beta,4\alpha}$ = 5.2, $J_{3\beta,2\alpha}$ = 5.2 Hz, H3β), 5.17 (1 H, dt, $J_{3'}{}_{,2'}$ = 15.3, $J_{3',4'}$ = 6.9 Hz, H3′), 5.43 (1 H, ddt, $J_{2',3'}$ = 15.3, $J_{2',1'}$ = 10.2, $J_{2'}{}_{,4'} \simeq$ 1 Hz, H2′), 7.49–7.81 (5 H, m, ArH). Anal. Calcd for $C_{23}H_{34}O_4S$: C, 67.95; H, 8.43. Found: C, 68.0; H, 8.5.

The third fraction, R_f 0.47, was a mixture of unchanged enone (8%) and the vinylic sulfone **31** (51 mg, 3.5%), and the fourth was a mixture of the carbonyl adducts **33** and **34** (125 mg, 9%).

1-(Methylsulfonyl)oct-2-ene (9) with But-2-en-4-olide. From the sulfone (*E*:*Z* > 97:3) (380 mg, 2.0 mmol) and the enone at −70 °C was obtained a yellow oil (480 mg), which was submitted to HPLC with 23:77 ethyl acetate–petroleum ether to give firstly unchanged sulfone (43 mg, 11%) and then *(1′RS,2′E,3SR)-3-[1′-(methylsulfonyl)oct-2′-enyl]butan-4-olide* (**42**) (205 mg, 37%): ^{1}H NMR δ 0.89 (3 H, m, H8′), 1.24–1.48 (6 H, m, H5′–H7′), 2.10–2.24 (2 H, m, H4′), 2.43 (1 H, dd, $J_{2\beta,2\alpha}$ = 18.0, $J_{2\beta,3}$ = 9.0 Hz, H2β), 2.64 (1 H, dd, $J_{2\alpha,2\beta}$ = 18.0, $J_{2\alpha,3}$ = 9.0 Hz, H2α), 2.87 (3 H, s, CH_3), 3.31 (1 H, ddddd, $J_{3,2\alpha}$ = 9.0, $J_{3,2\beta}$ = 9.0, $J_{3,1'}$ = 8.5, $J_{3,4\beta}$ = 8.0, $J_{3,4\alpha}$ = 7.5 Hz, H3), 3.52 (1 H, dd, $J_{1',2'}$ = 10.0, $J_{1',3}$ = 8.5 Hz, H1′), 4.24 (1 H, dd, $J_{4\beta,4}\alpha$ = 10.0, $J_{4\beta,3}$ = 8.0 Hz, H4β), 4.64 (1 H, dd, $J_{4\alpha,4\beta}$ = 10.0, $J_{4\alpha,3}$ = 7.5 Hz, H4α), 5.48 (1 H, ddt, $J_{2',3'}$ = 15.5, $J_{2',1'}$ = 10.0, $J_{2',4'}$ = 1.5 Hz, H2′), 5.94 (1 H, dt, $J_{3',2'}$ = 15.5, $J_{3',4'}$ = 7.0 Hz, H3′); HRMS calcd for $C_{13}H_{22}O_4S - SO_2CH_3$ 195.1384, found 195.1383.

The next product was *(1′RS,2′E,3RS)-3-[1′-(methylsulfonyl)-oct-2′-enyl]butan-4-olide* (**41**) (128 mg, 23%): ^{1}H NMR δ 0.89

(3 H, m, H8′), 1.24–1.48 (6 H, m, H5′–H7′), 2.11–2.19 (2 H, m, H4′), 2.48 (1 H, dd, $J_{2\beta,2\alpha}$ = 18.0, $J_{2\beta,3}$ = 8.5 Hz, H2β), 2.83 (1 H, dd, $J_{2\alpha,2\beta}$ = 18.0, $J_{2\alpha,3}$ = 8.5 Hz, H2α), 2.87 (3 H, s, CH_3), 3.35 (1 ddddd, $J_{3,2\alpha}$ = 8.5, $J_{3,2\beta}$ = 8.5, $J_{3,4\alpha}$ = 8.0, $J_{3,4\beta}$ = 7.5, $J_{3,1'}$ = 7.0 Hz, H3), 3.54 (1 H, dd, $J_{1',2'}$ = 10.5, $J_{1',3}$ = 7.0 Hz, H1′), 4.24 (1 H, dd, $J_{4\beta,4\alpha}$ = 10.0, $J_{4\beta,3}$ = 7.5 Hz, H4β), 4.41 (1 H, dd, $J_{4\alpha,4\beta}$ = 10.0, $J_{4\alpha,3}$ = 8.0 Hz, H4α), 5.51 (1 H, ddt, $J_{2',3'}$ = 15.5, $J_{2',1'}$ = 10.5, $J_{2',4'}$ = 1.2 Hz, H2′), 5.98 (1 H, dt, $J_{3',2'}$ = 15.5, $J_{3',4'}$ = 7.0 Hz, H3′); HRMS calcd for $C_{13}H_{22}O_4S - SO_2CH_3$ 195.1384, found 195.1380.

The most polar product was (*1′RS,2′E,3RS*)-*3*-[*3′*-(*methylsulfonyl*)-*1′*-*pentylprop*-*2′*-*enyl*]*butan*-*4*-*olide* (**40**) (104 mg, 19%): ^{1}H NMR δ 0.89 (3 H, m, H8′), 1.16–1.37 (6 H, m, H5′–H7′), 1.37–1.61 (2 H, m, H4′), 2.24–2.34 (1 H, m, H1′), 2.28 (1 H, dd, $J_{2\beta,2\alpha}$ = 17.5, $J_{2\beta,3}$ = 7.2 Hz, H2β), 2.62 (1 H ddddd, $J_{3,2\alpha}$ = 7.8, $J_{3,4\alpha}$ = 7.8, $J_{3,4\alpha}$ = 7.8, $J_{3,1'}$ = 7.5, $J_{3,2\beta}$ = 7.2 Hz, H3), 2.75 (1 H, dd, $J_{2\alpha,2\beta}$ = 17.5, $J_{2\alpha,3}$ = 7.8 Hz, H2α), 2.94 (3 H, s, CH_3), 3.98 (1 H, dd, $J_{4\beta,4\alpha}$ = 9.6, $J_{4\beta,3}$ = 7.8 Hz, H4β), 4.34 (1 H, dd, $J_{4\alpha,4\beta}$ = 9.6, $J_{4\alpha,3}$ = 7.8 Hz, H4α), 6.46 (1 H, d, $J_{3',2'}$ = 15.0 Hz, H3′), 6.66 (1 H, dd, $J_{2',3'}$ = 15.0, $J_{2',1'}$ = 10.0 Hz, H2′); HRMS calcd for $C_{13}H_{22}O_4S - SO_2CH_3$ 195.1384, found 195.1386.

The reaction was repeated in the presence of HMPA (1.5 equiv) and gave a product mixture containing less than 2% of the vinylic adduct **40**. The major products were the allylic adducts **42** (236 mg, 43%) and **40** (158 mg, 29%).

4-(*tert*-Butylsulfonyl)-2-methylpent-2-ene (10) with (i) Cyclopentenone. The sulfone (349 mg, 1.71 mmol) was deprotonated with LDA (1.88 mmol) containing 2,2′-bipyridyl in THF (30 mL) at −70 °C under nitrogen and then treated with the enone (157 mg, 1.88 mmol). The mixture was worked up immediately to give after flash chromatography with 20:80 ethyl acetate–petroleum ether (*2′E*)-*3*-[*1′,1′*-*dimethyl*-*3′*-(*tert*-*butylsulfonyl*)*but*-*2′*-*enyl*]*cyclopentanone* (**43**) (406 mg, 83%) as a pale yellow oil: ^{1}H NMR δ 1.23 (6 H, s, 2 CH_3), 1.36 (9 H, s, *t*-Bu), 1.65–2.45 (7 H, m, H2–H5), 2.21 (3 H, d, $J_{4',2'}$ = 1.5 Hz, CH_3), 6.64 (1 H, q, $J_{2',4'}$ = 1.5 Hz, H2′). Anal. Calcd. for $C_{15}H_{26}O_3S$: C, 62.9; H, 9.1. Found: C, 62.8; H, 9.4.

(ii) Cyclohex-2-enone. The sulfone (369 mg, 1.22 mmol) in THF at −70 °C was deprotonated with LDA (1.35 mmol). The solution was warmed to −15 °C and treated with the enone (130 mg, 1.35 mmol). The reaction mixture was quenched after 5 min at −15 °C to give a pale yellow oil, purification of which by preparative layer TLC with 1:1 ethyl acetate–petroleum ether gave (*2′E*)-*3*-[*1′,1′*-*dimethyl*-*3′*-(*tert*-*butylsulfonyl*)*but*-*2′*-*enyl*]*cyclohexanone* (**44**) (260 mg, 72%) as a colorless oil: ^{1}H NMR δ 1.081 (3 H, s, CH_3), 1.091 (3 H, s, CH_3), 1.36 (9 H, s *t*-Bu), 1.6–2.5 (9 H, m, H2–H6), 2.19 (3 H, d, $J_{4',2'}$ = 1.2 Hz, H4′), 6.63 (1 H, m, H2′). Anal. Calcd for $C_{16}H_{28}O_3S$: C, 64.0; H, 9.4. Found: C, 64.1; H, 9.6.

Also isolated was the nonpolar allene, *3*-(*1′,1′*-*dimethylbuta*-*2′,3′*-*dienyl*)*cyclohexan*-*1*-*one* (63 mg, 17%) as a colorless oil:[33] ^{1}H NMR δ 1.012 (3 H, s, CH_3), 1.025 (3 H, s, CH_3), 1.2–1.65 (m) and 1.94–2.5 (m) (9 H, H2–H6), 4.74 (2 H, d, H4′), 5.02 (1 H, dd, $J_{2',4'} \simeq 6.6$, $J_{2',4'} \simeq 6.6$ Hz, H2′); HRMS calcd for $C_{12}H_{18}O$ 178.1357, found 178.1356.

(33) Related allenes form under similar conditions from 1-methylvinyl sulfoxides.[12] Formation of allenes from 1-methylvinyl sulfones as in the present case has not previously been observed.

From the sulfone (391 mg, 1.92 mmol) and the enone (200 mg, 2.1 mmol) in THF containing HMPA (1.03 g, 5.76 mmol) at −70 °C was obtained a yellow oil, a ^{1}H NMR spectrum of which indicated an 81:19 mixture of two diastereomers, and small amounts of other, unidentified products. A solution of the oil in ethyl acetate–petroleum ether deposited prisms, mp 93–94.5 °C, of a single stereoisomer of *3*-[*1′*-(*tert*-*butylsulfonyl*)-*1′,3′*-*dimethylbut*-*2′*-*enyl*]*cyclohexanone* (**45**) (351 mg, 61%): ^{1}H NMR δ 1.081 (3 H, s, CH_3), 1.091 (3 H, s, CH_3), 1.6–2.5 (9 H, m, H2–H6), 2.19 (3 H, d, $J_{4',2'}$ = 1.2 Hz, H4′), 6.63 (1 H, m, H2′). Anal. Calcd for $C_{16}H_{28}O_3S$: C, 64.0; H, 9.4. Found: C, 64.2; H, 9.6.

Rearrangement of (i) 1-[1′-[(4-Methylphenyl)sulfonyl]-but-2′-enyl]cyclohex-2-en-1-ol (22). A solution of the 68:32 mixture of diastereomers of the carbonyl adduct **22** (429 mg, 1.41 mmol) in THF (30 ml) at −70 °C containing a few crystals of 2,2′-bipyridyl was treated slowly with a solution of LDA until onset of permanent coloration due to the indicator. The reaction mixture was warmed to 0 °C when it was stirred for 2.5 h prior to quenching with aqueous ammonium chloride. The yellow oil obtained after workup was purified by preparative layer TLC with 40:60 ethyl acetate–petroleum ether to give an 89.5:10.5 mixture of the diastereomers **23** and **24** (330 mg, 77%).

(ii) 1-[1′-(Phenylsulfonyl)but-2′-enyl]cyclohex-2-en-1-ol (28). A solution of the 75:25 mixture of diastereomers of the carbonyl adduct **28** (128 mg, 0.44 mmol) in THF (20 mL) at −70 °C was treated with butyllithium (0.45 mmol). The resulting solution was warmed to 0 °C when it was stirred for 1.5 h before being quenched with aqueous ammonium chloride. The yellow oil obtained after workup was purified by preparative layer TLC with 40:60 ethyl acetate–petroleum ether to give an 82:18 mixture of the vinyl sulfoxides **29** and **30** (95 mg, 74%).

Acknowledgment. We thank the Australian Research Council for support of this work.

Registry No. (*E*)-**6**, 68276-71-1; (*Z*)-**6**, 72592-55-3; (*E*)-**7**, 72863-24-2; (*Z*)-**7**, 89249-38-7; (*E*)-**8**, 91940-09-9; (*Z*)-**8**, 86823-71-4; (*E*)-**9**, 119010-85-4; (*Z*)-**9**, 119011-14-2; (±)-**10**, 119038-57-2; (±)-**11**, 930-30-3; (±)-**12**, 70834-92-3; (±)-**13**, 930-68-7; (±)-**14**, 497-23-4; (±)-**15**, 119010-86-5; (±)-**16**, 119010-87-6; (±)-**17** (isomer 1), 119010-88-7; (±)-**17** (isomer 2), 119010-89-8; (±)-**18** (isomer 1), 119010-90-1; (±)-**18** (isomer 2), 119010-91-2; (±)-**19**, 119038-58-3; (±)-**20**, 119010-92-3; (±)-**21**, 119068-47-2; (±)-**22** (isomer 1), 119010-93-4; (±)-**22** (isomer 2), 119010-94-5; (±)-**23**, 119010-95-6; (±)-**24**, 119010-96-7; (±)-**25**, 119010-97-8; (±)-**26**, 119010-98-9; (±)-**27** (isomer 1), 119010-99-0; (±)-**27** (isomer 2), 119011-00-6; (±)-**28** (isomer 1), 119011-01-7; (±)-**28** (isomer 2), 119011-02-8; (±)-**29**, 119011-03-9; (±)-**30**, 119011-04-0; (±)-**31**, 119011-05-1; (±)-**32**, 119068-48-3; (±)-**33**, 119011-06-2; (±)-**34**, 119068-49-4; (±)-**35**, 119011-07-3; (±)-**36**, 119324-33-3; (±)-**40**, 119011-09-5; (±)-**41**, 119038-41-4; (±)-**42**, 119011-10-8; (±)-**43**, 119011-11-9; (±)-**44**, 119011-12-0; (±)-**45** (isomer 1), 119011-08-4; (±)-**45** (isomer 2), 119011-13-1.

Supplementary Material Available: Commentary on determination of relative configuration and preferred conformers for compounds **20**, **21**, **33**, and **34** and characterization data, including IR, ^{13}C NMR, and mass spectral data, for new compounds (8 pages). Ordering information is given on any current masthead page.