A General Synthesis of Methylenecyclopentanes by a Stereoselective [3 + 2] Approach

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The [3 + 2] cyclopentanation involving 3-(phenylsulfonyl)-2-(bromomethyl)-1-propene (**1**) and representative (*E*) α,*β*-unsaturated acyclic esters and ketones has been studied. High yields and complete stereoselectivity were observed in all reactions leading to tri- or tetrasubstituted methylenecyclopentanes. The *anti*-diastereoselectivity in the first, Michael addition step is rationalized by a chelation-controlled transition state in which MO interactions of the two π systems are involved. The Michael reactions of methallyl sulfone **8** with (*E*) enoates in the absence and presence of HMPA confirms the influence of chelation on the diastereomeric ratio of adducts. Cyclopentanations involving **1** with cyclohexenone, 2(5*H*)-furanone, and 5,6-dihydro-2-pyranone, respectively, were also studied with emphasis on the factors influencing the stereochemical outcome of the annulation process.

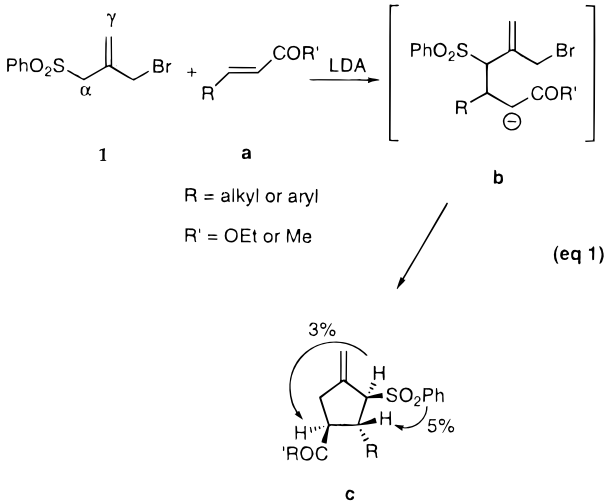
Introduction

Five-membered carbocycles are important building blocks for the synthesis of cyclopentanoid natural products. Among the growing number of methodologies developed during recent years for the construction of cyclopentanes, the [3 + 2] strategy has been widely explored because it offers the possibility of forming two carbon−carbon bonds under the same reaction conditions.[2,3] Practical interest in such methodology may depend on several factors such as (a) the scope of the process, (b) ready availability of utilized substrates, (c) simplicity of experimental procedures, (d) regio- and stereoselectivities of the process, and (e) eventual possibility of enantioselective construction of cyclopentanes.[4] Among the reported [3 + 2] cyclopentanations, many of which fail to fulfill several of the above conditions, the utilization of trimethylenemethane (TMM) and its organometallic complexes as the three-carbon moiety deserves special attention.[5,6]

We recently investigated the utilization of a TMM equivalent, which does not undergo self-destruction under basic conditions, namely, 3-(phenylsulfonyl)-2-(bromomethyl)-1-propene (**1**), in 3 + 2 anionic cyclopentanations. We reported on the Michael-initiated ring closure (MIRC)[7] involving **1** with nitroolefins[8] and 2-(phenylsulfonyl) enones,[9] respectively, as acceptors. In this paper we report the results of tandem MIRC of **1** with acyclic α,*β*-unsaturated esters and ketones leading to cyclopentanation in a process characterized by high effectivity and diastereoselectivity.[10,11] A rationalization of the stereochemical outcome of these reactions is proposed. The scope of this [3 + 2] process was further extended by its application to α,*β*-unsaturated lactones and cyclic enones.

Results and Discussion

Cyclopentanations with Acyclic Acceptors. The readily prepared bromo allyl sulfone **1** was deprotonated by lithium diisopropylamide (LDA) in THF solution at low temperature (−95 °C). Addition of representative acyclic (*E*) α,*β*-unsaturated esters and ketones to lithiated **1** resulted in a rapid and effective conversion into the corresponding methylenecyclopentanes via conjugate addition followed by ring closure (eq 1 and Table 1). All



[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1996.

(1) Synthetic Methods. 47. For part 46, see: Hassner, A.; Namboothiri, I. N. N. *J. Organomet. Chem.* In press.

(2) For a review, see: Hudlicky, T.; Price, J. D. *Chem. Rev.* **1989**, *89*, 1467.

(3) For [3 + 2] cyclopentanations (not included in ref 2), see, *inter alia*: Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 389 and references therein. Feldman, K. S.; Romanelli, A. L.; Ruckle, R. E.; Miller, R. F. *J. Am. Chem. Soc.* **1988**, *110*, 3300. Curran, D. P.; Chen, M. H. *J. Am. Chem. Soc.* **1987**, *109*, 6558. Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165. Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1989**, *111*, 7285. Lee, T. V.; Richardson, K. A.; Ellis, K. L.; Visani, N. *Tetrahedron* **1989**, *45*, 1167. Panek, J. S.; Jarom, N. F. *J. Org. Chem.* **1993**, *58*, 2345. Knölker, H. J.; Graf, R. *Synlett* **1994**, *131*. Hudlicky, T.; Heard, N. E.; Fleming, A. *J. Org. Chem.* **1990**, *55*, 2570. Molander, G. A.; Schubert, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 4683 and references therein.

(4) Our results in this direction will be reported elsewhere.

(5) For a review, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.

(6) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1988**, *29*, 201. Trost, B. M.; Mignani, S. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1988**, *110*, 1602. Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487.

(7) For this term, see: Little, D. R.; Dawson, J. R. *Tetrahedron Lett.* **1980**, *21*, 2609.

(8) Ghera, E.; Yechezkel, T.; Hassner, A. *J. Org. Chem.* **1993**, *58*, 6717.

(9) Yechezkel, T.; Ghera, E.; Ostercamp, D.; Hassner, A. *J. Org. Chem.* **1995**, *60*, 5135.

(10) For a preliminary report of a part of this work, see: Ghera, E.; Yechezkel, T.; Hassner A. *Tetrahedron Lett.* **1990**, *25*, 3653.

(11) Subsequent to our preliminary report (ref 10), a MIRC process involving the dilithiated chloro analog of **1** was reported to give stereomeric mixtures of methylcyclopentenes: Najera, C.; San Sano, J. Mo. *Tetrahedron* **1994**, *50*, 3491.

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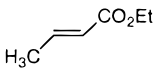
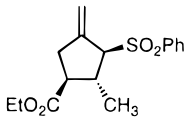
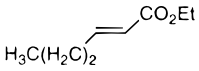
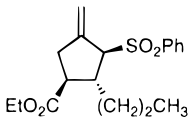
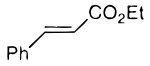
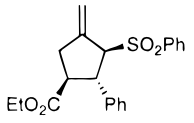
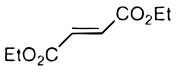
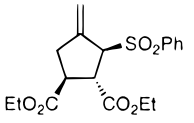
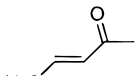
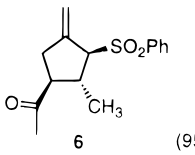
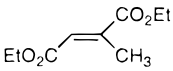
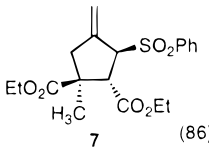
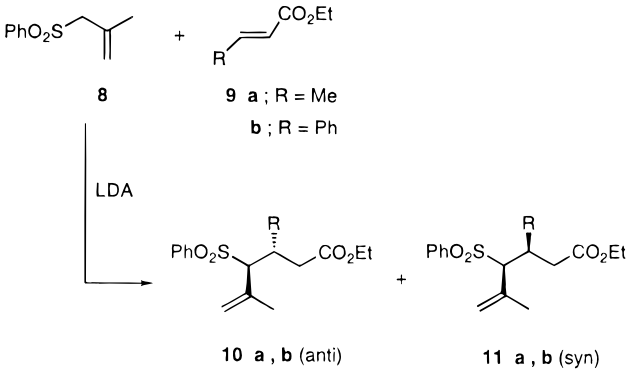
Table 1. Cyclopentanations by Reaction of 1 with Acyclic (*E*) Acceptors

entry	acceptor	reaction time (at -95°C)	product (yield %)
1		5 min	 **2** (93)
2		10 min	 **3** (93)
3		20 min	 **4** (92)
4		10 min	 **5** (81)
5		15 min	 **6** (95)
6		10 min	 **7** (86)

additions occurred in a regioselective manner at the α-phenylsulfonyl terminus of the allylic carbanion and were characterized by complete stereoselectivity at the three stereogenic centers of the resulting methylenecyclopentanes **2**−**7**. The stereochemical assignments for the stereohomogeneous products were made on the basis of spectral evidence and consistent NOE data shown in eq 1. The presence of additional substitution in the acceptor, leading to the tetrasubstituted methylenecyclopentane derivative **7** (entry 6), did not affect the effectivity and stereoselectivity of the cyclopentanation. Open-chain intermediates formed in the conjugate addition step could not be detected even when we attempted to slow down the ring closure, e.g., by addition of hexane to the reaction mixture. Similarly, very fast quenching of the reaction at low temperature provided solely cyclized product **2**−**7** together with unreacted sulfone **1**. It can therefore be assumed that the ring closure step occurs faster than the rate-determining Michael addition to form b (eq 1). The formation of *trans*−*trans* products **2**−**6** requires that the first step, Michael addition to a, lead to the *anti*[12] diastereomer of b. The outcome of the ring closure step to c can be thermodynamically rationalized. The complete stereoselectivity in these high-yield cyclopentanations was substantiated by ^{1}H NMR evidence (absence of alternative vinylic protons in the spectrum of the crude products, with 1% limit of detection).

Table 2. Reactions of 8 with (*E*) Enoates (9a,b). Influence of HMPA on the Diastereomeric Ratio[a]



entry	acceptor	anti / syn ratio	total yield (%)
1	**9a**	85 : 15	92
2	**9a** , HMPA	40 : 60	92
3	**9b**	100 : 0	87
4	**9b** , HMPA	20 : 80	55[b]

[a] Standard reaction conditions (−95 °C, 15 min) were used except for entry 4 (−95 to −70 °C, 30 min). [b] 24% of unreacted ethyl cinnamate was recovered.

In order to rationalize the *anti*-diastereoselective[12] outcome of the initial conjugate addition step, the well-documented sensitivity of Michael reactions to the steric environment[13] should be taken into account along with chelation control in the transition state (TS), via coordination of the lithium counterion with the oxygens of the sulfone and the carbonyl group.[14]

Ion pair dissociation, favored by addition of a solvating agent (HMPA) to the reaction mixture, should provide information about the influence of the chelation factor in the TS, for instance, by significantly altering the diastereomeric ratio of products. Since the lithiated bromo sulfone **1** in THF solution was unstable in the presence of HMPA, we examined the analogous methallyl sulfone **8** in conjugate additions with ethyl (*E*)-crotonate (**9a**) and ethyl (*E*)-cinnamate (**9b**). Indeed, the *anti*/*syn* diastereomeric ratio (**10**:**11**) was significantly affected in the presence of HMPA, with the preference shifting drastically in favor of the *syn*-diastereomer (Table 2). The preponderance of a chelated TS was thus substantiated. It is noteworthy that in the presence of HMPA the conjugate addition of **8** to ethyl cinnamate, via a non-

(12) *Syn* and *anti* designations are based on the extended form including both anion-stabilizing groups (SO_2 and C=O). See: Oare, D. A.; Heathcock, C. H. In *Topics in Stereochemistry;* Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1989; Vol. 19, p 227. In an early report (ref 10) we made opposite designations for *syn* and *anti*. For monocyclic products (such as **15**), the designations *erythro* and *threo* have been used in order to avoid misunderstandings.

(13) Chapdelaine, M. J.; Hulce, M. *Org. React.* **1990**, *38*, 225.

(14) Binns, M. R.; Haynes, R. K.; Katsifis, A. G.; Schober, P. A.; Vonwiller, S. C. *J. Org. Chem.* **1989**, *54*, 1960.

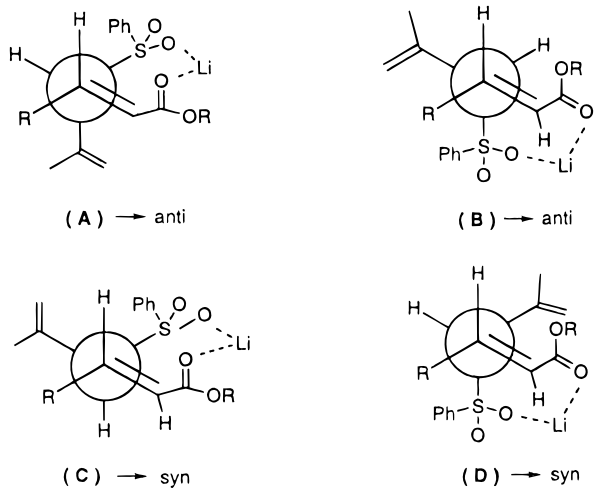


Figure 1.

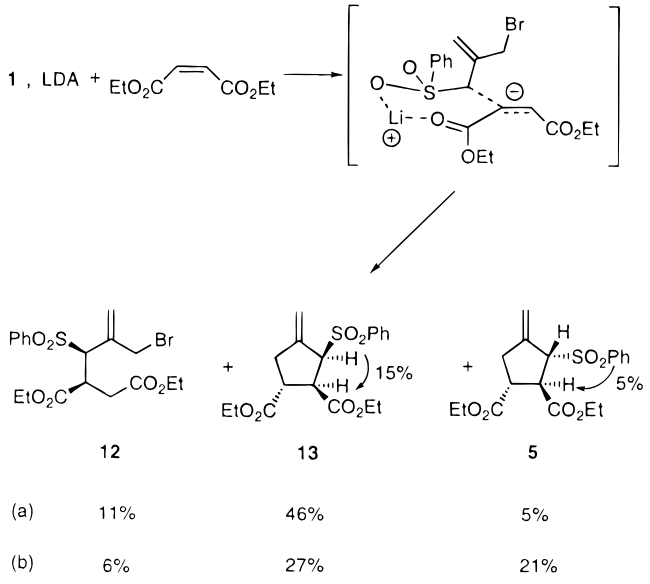
chelated TS, is slower and less effective (entry 4) than in the chelation-assisted addition (entry 3).

It is reasonable to assume that, as for sulfone **8**, the analogous reactions of bromo sulfone **1** with acyclic (*E*) unsaturated carbonyl compounds likewise involve a chelated TS. However, the chelation factor alone proved insufficient to account for the stereochemical outcome of conjugate additions involving **1** and **8**, respectively. Thus, consideration of the four "cyclic" TS (A−D, Figure 1) leads at first glance to the conclusion that the TS (C) should be the sterically favored one, having *anti*-positioned hydrogens at the two vicinal stereocenters. However, (C) leads to the *syn*-diastereomer. The preferential formation (as in **10a**) or the sole formation (as in **10b** and **2**−**7**) of the *anti*-diastereomer can be rationalized by considering an additional factor, namely, a secondary orbital interaction involving a HOMO−LUMO complex between the (*E*) enoate moiety and the allylic anion in the transition state. Calculations have shown that such interactions resulting from overlap of the two π systems, may compensate for the repulsions due to a hindered approach of reactants.[15] Careful inspection of models visualizes that such overlap takes place better in TS (A) than in (D). Moreover, in TS (A) the "cisoid" chelation with the counterion leading to *anti*-addition should be favored over the "transoid" chelation in TS (D).

The Li−O coordination can also have a negative influence on the outcome of conjugate additions as evidenced in reactions with (*Z*) enoates: in sharp contrast to the effectivity of cyclopentanations with (*E*) acceptors, the reactions of **1** with (*Z*)-crotonate and -cinnamate, respectively, did not afford the desired conjugate adducts and resulted mainly in polymerization. The association of the lithiated reagent with the ester group is probably hindering the conjugate attack on the same (R-substituted) face of the double bond. The reaction of **1** with diethyl maleate led however to cyclopentanation (Scheme 1): chelation involving the sulfone and one of the carboxylate groups facilitates the attack on the unsaturated carbon nearest to the site of chelation with a resulting *cis*-relationship between the phenylsulfonyl group and the vicinal carboxylate (15% NOE for the related protons in **13**). The minor product (**5**) probably results from equilibration: increase in the time and

(15) Sevin, A.; Tortajada, J.; Pfau, M. *J. Org. Chem.* **1986**, *51*, 2671.

Scheme 1.[a] Base-Induced Reaction of 1 with Diethyl Maleate



	12	13	5
(a)	11%	46%	5%
(b)	6%	27%	21%

[a] Reaction conditions: (a) −95 to −50 °C, 1 h; (b) −95 to −30 °C, 1.5 h.

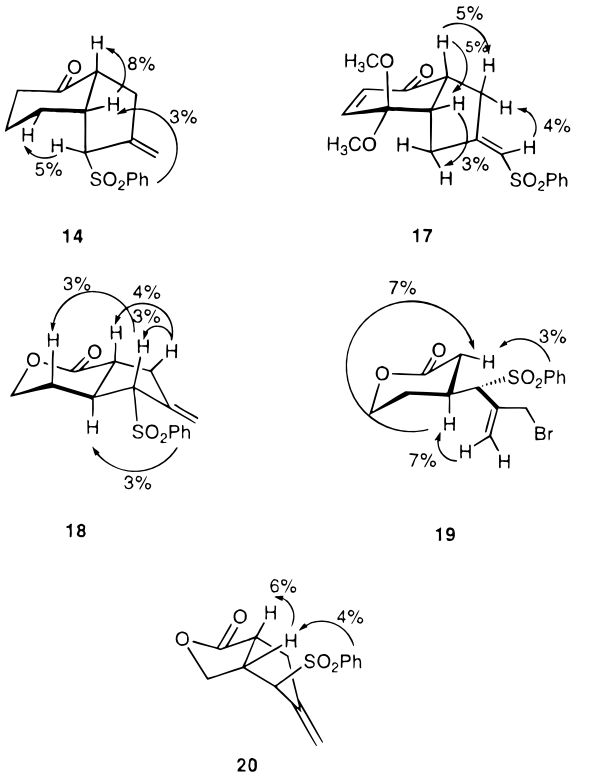
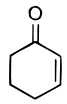
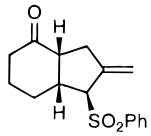
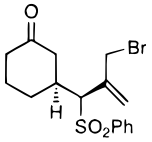
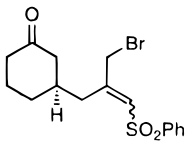
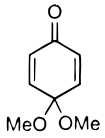
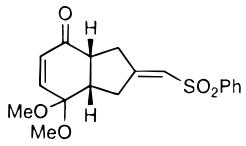
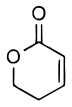
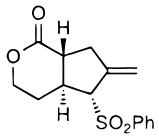
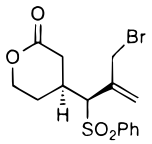
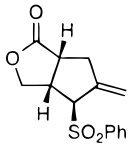
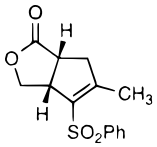
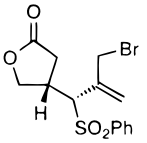


Figure 2. Conformational and stereochemical data for compounds **14** and **17**−**20**.

temperature of the reaction resulted in more equilibration to **5**, as shown in Scheme 1. The ring closure to **13** is not as rapid as for (*E*) enoates and the open-chain adduct **12** also was isolated. Its tentatively assigned stereochemistry can be anticipated because the other diastereomer would close at once to **5**, as observed in reactions of **1** with diethyl fumarate (Table 1, entry 4).

The conjugate addition step in the reactions summarized in Table 1 seems kinetically controlled because under the given reaction conditions neither base-induced equilibration nor a retro-Michael reaction should account

Table 3. Cyclopentannulations by Reaction of 1 with Cyclic Acceptors

entry	acceptor	reaction conditions (temp., time)	products (yields %)
1		-95° to -50°C, 1h	 **14** (48%);  **15** (12%);  **16** (10%)
2		-95° to -50°C, 1h	 **17** (65%)
3		-95°C, 30 min	 **18** (66%);  **19** (12%)
4		-95°C, 15 min	 **20** (69%);  **21** (7%);  **22** (8%)

for the formation of a sole diastereomer. Hence the slow equilibration observed for **13** → **5** (Scheme 1, b).

Cyclopentanation with Cyclic Acceptors. Cycloalkenones and α,β-unsaturated lactones reacted in a similar manner by a MIRC process with bromo sulfone **1** to afford bicyclic products (Table 3). The regiochemical outcome, such as with acyclic acceptors, is characterized by the conjugate addition of the allylic carbanion reacting primarily from the α-terminus of the allyl sulfone, except for the case when the hindering group on the acceptor (4,4-dimethoxycyclohexadienone, entry 2) forced the addition via the less hindered γ-terminus to provide **17**, a potentially interesting synthetic intermediate. The stereochemical assignments for **17** rely on NOE data (Figure 2). Previously reported reactions of other allylic sulfones with cyclohexenone at low temperature and in the absence of HMPA afforded mainly 1,2-carbonyl addition products.[14,16] We did not detect such products, but the selectivity of this conjugate addition was not as high as with acyclic acceptors: along with **14**, originating from the cyclization of the *erythro*-diastereomeric adduct, minor amounts of open-chain adduct **15**, with the tentatively assigned *threo*-configuration,[12,17] and of the vinylic sulfone **16** (a γ-adduct) were also isolated. The assigned *cis*-fusion for the hydrindanone derivative **14** (entry 1) is based on NOE data (Figure 2).

Cyclopentanations of unsaturated lactones (entries 3 and 4, Table 3) were more effective and afforded **18** and **20**, respectively, as the major products. The *trans*-fusion for **18** as well as the expected *cis*-fusion in **20** was secured by NOE data (Figure 2). *Threo*-configuration was assigned for the minor adduct **19** (Figure 2) and for **22** (by analogy).

As mentioned for acyclic acceptors, the Z geometry of the double bond should make the intermediacy of a cyclic TS in which the sulfone and carbonyl oxygens are coordinated via the lithium counterion more difficult, and the same should hold for (*Z*) double bonds in cyclic systems. Haynes and co-workers[14] assumed that an "extended" ten-membered cyclic TS (via γ-attack) is conformationally less viable for conjugate additions of allylic sulfones to cyclohexenone than to cyclopentenone. An eight-membered transition state, as required for the formation of adducts **14**, **15**, and **18**−**22**, via an α-attack, would appear even more hindered. We assume, therefore, that steric effects and MO interactions (π−π attraction) are largely responsible for the stereochemical outcome of conjugate additions with cyclic acceptors. The TS (E), which is less hindered than (F), leads to the prevalence of the *erythro*-diastereomer (Figure 3).

The role of possible Li−O coordination in the above reactions was examined by using again methallyl sulfone **8** as the donor which enables the conjugate additions to be carried out in the presence of HMPA (Table 4). Interestingly, only 25% of adducts along with recovered

(16) Hirama, M. *Tetrahedron Lett.* **1981**, *22*, 1905.
(17) Steric obstruction between the cyclohexane ring and the phenylsulfonyl group probably prevent the cyclization of **15**.

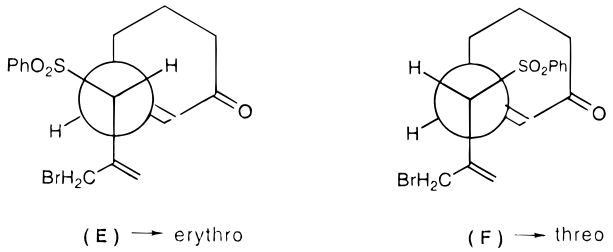
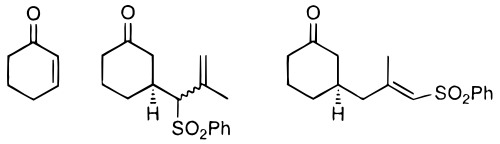
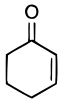
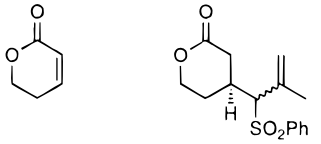
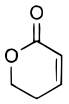


Figure 3.

Table 4. Influence of HMPA on the Outcome of Reactions of 8 with Cyclic Acceptors[a]

entry	acceptor	products (yield %)
1		**23** a , erythro(9%) **24** (7%) b , threo(9%)
2	 + HMPA	**23** a , (61%) b , (20%)
3		**25** a , erythro (63%) b , threo (22%)
4	 +HMPA	**25** a , (71%) b , (12%)

[a] All reactions were conducted under the same conditions (−95 °C, 20 min).

starting material were obtained in the reaction with cyclohexenone (entry 1), whereas in the presence of HMPA and under the same conditions this reaction was found as effective as previously reported for propenyl sulfone.[16] Adduct **23** was obtained as a 3:1 *erythro/threo* mixture of diastereomers **23**a and **23**b. In contrast to cyclohexenone, the yields obtained in the reaction with 5,6-dihydro-2-pyranone (entries 3 and 4) revealed only slight dependence on the presence or absence of HMPA, although differences in the ratio of diastereomers **25a** and **25b** were observed. The improvement of reactivity in the latter reaction due to Li coordination with the noncarbonylic oxygen seems therefore minimal. However, the presence of ring oxygen in an enone has been shown previously to improve reactivity in conjugate additions[18] due to the lowering of the LUMO energy by interaction with the π system.[19] The stereochemical

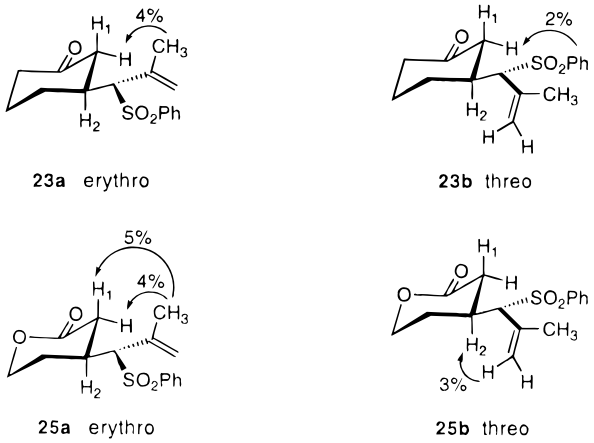


Figure 4. Stereochemical Data for Compounds **23a,b** and **25a,b**

assignments for **23a,b** and **25a,b** (Figure 4) are based on NOE data in conjunction with *J* values: diaxial coupling ($J_{1,2}$ = 12 Hz) and *anti*-arrangement of the protons at the stereogenic centers (H-2 and C*H*SO_2Ph, see Experimental Section for the corresponding *J* values).

Conclusion

The foregoing results of base-induced additions of allylic bromo sulfone **1** to acyclic (*E*) enoates and enones demonstrate that the cyclopentanations leading to trisubstituted methylenecyclopentanes via *anti*-adducts take place with excellent effectivity and diastereoselectivity. Molecular orbital $\pi-\pi$ interactions need to be taken into account along with a "cyclic" chelated transition state in order to rationalize the *anti*-diastereoselectivity observed in the conjugate addition step. Reactions of a halogen-devoid analog of **1**, namely, methallyl sulfone **8** with (*E*) enoates, in the presence of HMPA, gave rise to drastic changes of the diastereomeric ratio, thus confirming the role of chelation. Although the (*Z*) geometry of acyclic acceptors proved unfavorable for performing the studied Michael additions, cyclopentanations were successful when cyclohexenone and α,β-unsaturated lactones were used as the acceptors for **1**. The presence of the additional oxygen in lactones had a favorable effect on the yields of additions involving **1** and **8**, respectively.

Experimental Section

General experimental techniques and analytical measurements were applied as previously described.[20] Melting points are uncorrected. Mass spectra (CI) were recorded at 60 eV. Methallyl sulfone **8** was prepared as reported.[21] Reactions with cooling at −95 °C were performed using a mixture of liquid nitrogen and MeOH.

2-(Bromomethyl)-3-(phenylsulfonyl)-1-propene (1). A mixture containing 2-(chloromethyl)-3-(phenylsulfonyl)-1-propene[22] (5 g, 0.02 mol) and sodium bromide (2.06 g, 0.02 mol) in 120 mL of 2:1 (v/v) DMF:CH_2Br_2 was stirred overnight at 100 °C (external temperature, preheated oil bath). After removal of the solvents under reduced pressure, the residue was dissolved in CH_2Cl_2. The organic layer washed with water (3 × 50 mL) and brine, dried over $MgSO_4$, and evaporated under reduced pressure to give a white solid. Recrystallization

(18) Frazer-Reid, B.; Holder, N. L.; Hicks, D. R.; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3986.
(19) Frazer-Reid, B.; Underwood, R.; Osterhout, M.; Grossman, J. A.; Liotta, D. L. *J. Org. Chem.* **1986**, *51*, 2152.
(20) Ghera, E.; Yechezkel, T.; Hassner, A. *J. Org. Chem.* **1990**, *55*, 5977.
(21) Trost, B. H.; Schmuff, N. S. *J. Am. Chem. Soc.* **1985**, *107*, 396.
(22) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1987**, *28*, 6053.

(diisopropyl ether) gave the pure product (**1**), stable at ambient temperature (4.4 g, 80%): mp 53 °C; ^{1}H NMR δ 7.99−7.82 (m, 2H), 7.74−7.49 (m, 3H), 5.49 (s, 1H), 5.00 (s, 1H), 4.13 (s, 2H), 3.79 (s, 2H); ^{13}C NMR δ 137.95 (s), 133.88 (d), 133.71 (s), 129.08 (d, 2 × CH), 128.23 (d, 2 × CH), 124.45 (t), 59.65 (t), 35.02 (t); MS (CI/NH_3) *m*/*z* 294, 292 (MNH_4^+, 100, 98), 248 (8).

Reactions of Bromo Sulfone 1 with (*E*) Unsaturated Acyclic Carbonyl Compounds. General Procedure. To a stirred solution of LDA, prepared at 0 °C from 0.17 mL (1.3 mmol) of diisopropylamine and 0.83 mL of *n*-BuLi (1.25 mmol, 1.5 M solution in hexane) in 5.5 mL of THF, was added dropwise at −95 °C a solution of **1** (385 mg, 1.4 mmol)[23] in 4.5 mL of THF. After the solution was stirr for 10 min at the above temperature, the unsaturated carbonyl compound was added (1 mmol) in 2.3 mL of THF. After completion of the reaction (see Table 1), the reaction mixture was quenched with aqueous (20%) AcOH, poured into water, and extracted with CH_2Cl_2. The extracts were washed successively with saturated $NaHCO_3$ solution and water, dried ($MgSO_4$), and evaporated under reduced pressure. All the products were purified by column chromatography over silica gel to afford the yields indicated in Table 1.

Ethyl (1*β*,2α,3*β*)-2-Methyl-4-methylene-3-(phenylsulfonyl)cyclopentanecarboxylate (2). Elution: EtOAc/petroleum ether 1:3. **2**: ^{1}H NMR δ 7.98−7.79 (m, 2H), 7.75−7.65 (m, 1H), 7.60−7.50 (m, 2H), 5.25 (ddt, *J* = 3, 2, 1 Hz, 1H), 5.13 (ddt, *J* = 3, 2, 1 Hz, 1H), 4.17 (q, *J* = 7 Hz, 2H), 3.61 (dq, *J* = 7, 2 Hz, 1H), 2.81 (ddqd, *J* = 10, 8, 7, 0.5 Hz, 1H), 2.55−2.30 (m, 3H), 1.28 (t, *J* = 7 Hz, 3H), 1.13 (d, *J* = 7 Hz, 3H); ^{13}C NMR δ 172.75 (s), 141.79 (s), 137.07 (s), 133.77 (d), 129.69 (d, 2 × CH), 128.92 (d, 2 × CH), 115.45 (t), 74.53 (d), 60.77 (t), 50.79 (d), 39.67 (d), 38.19 (t), 19.60 (q), 14.20 (q); MS (CI/CH_4) *m*/*z* 309 (MH^+, 55), 263 (100), 169 (60). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.54. Found: C, 62.57; H, 6.62.

Ethyl (1*β*,2α,3*β*)-4-Methylene-3-(phenylsulfonyl)-2-propylcyclopentanecarboxylate (3). Elution: EtOAc/petroleum ether 1:5. **3**: ^{1}H NMR δ 7.95−7.86 (m, 2H), 7.70−7.62 (m, 1H), 7.59−7.51 (m, 2H), 5.19 (td, *J* = 3, 1.5 Hz, 1H), 4.97 (td, *J* = 3, 1.5 Hz, 1H), 4.17, 4.10 (ABq of q, J_{gem} = 10.5 Hz, J_{vic} = 7 Hz, 2H), 3.60 (dq, *J* = 6, 1.5 Hz, 1H), 2.97 (quin d, *J* = 7, 2 Hz, 1H), 2.55−2.33 (m, 3H), 1.51−1.40 (m, 2H), 1.24 (t, *J* = 7 Hz, 3H), 1.32−1.18 (m, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 177.33 (s), 142.24 (s), 136.92 (s), 133.54 (d), 129.62 (d, 2 × CH), 128.69 (d, 2 × CH), 115.24 (t), 73.91 (d), 60.60 (t), 49.10 (d), 43.25 (d), 38.12 (t), 37.50 (t), 19.71 (t), 13.96 (q), 13.79 (q); MS (CI/CH_4) *m*/*z* 337 (MH^+, 100), 291 (79), 263 (53), 195 (68). Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 63.98; H, 6.99; S, 9.71.

Ethyl (1*β*,2α,3*β*)-4-methylene-2-phenyl-3-(phenylsulfonyl)cyclopentanecarboxylate (4). Elution: EtOAc/petroleum ether 1:5. **4**: ^{1}H NMR δ 7.82−7.76 (m, 2H), 7.58−7.50 (m, 1H), 7.46−7.38 (m, 2H), 7.20−7.09 (m, 3H), 7.01−6.94 (m, 2H), 5.35 (dt, *J* = 2, 1 Hz, 1H), 5.19 (dt, *J* = 3, 1.5 Hz, 1H), 4.14 (qd, *J* = 7, 2 Hz, 1H), 4.04 (qd, *J* = 7, 1 Hz, 2H), 3.93 (dd, *J* = 10, 7 Hz, 1H), 2.91 (ddd, *J* = 12, 10, 7 Hz, 1H), 2.81−2.61 (m, 2H), 1.13 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 172.18 (s), 141.71 (s), 141.19 (s), 137.28 (s), 133.60 (d), 129.28 (d, 2 × CH), 128.83 (d, 2 × CH), 128.54 (d, 2 × CH), 127.29 (d, 2 × CH), 126.99 (d), 115.72 (t), 75.09 (d), 60.80 (t), 52.29 (d), 49.66 (d), 38.68 (t), 14.08 (q); MS (EI) *m*/*z* 371 (MH^+, 4), 325 (6), 228 (76), 155 (100).

Ethyl (1*β*,2α,3*β*)-2-(Ethoxycarbonyl)-4-methylene-3-(phenylsulfonyl)cyclopentanecarboxylate (5). Elution: EtOAc/petroleum ether 1:4. **5**: mp 56−58 °C; ^{1}H NMR δ 7.96−7.89 (m, 2H), 7.70−7.63 (m, 1H), 7.60−7.53 (m, 2H), 5.32 (td, *J* = 2, 1 Hz, 1H), 5.21 (td, *J* = 2, 1 Hz, 1H), 4.44 (dq, *J* = 7, 2 Hz, 1H), 4.17 (q, *J* = 7 Hz, 2H), 4.04, 3.96 (ABq of q, J_{gem} = 10.5 Hz, J_{vic} = 7 Hz, 2H), 3.69 (dd, *J* = 10, 7 Hz, 1H), 2.93 (ddd, *J* = 12, 10, 7 Hz, 1H), 2.67 (bdd, *J* = 15, 7 Hz, 1H), 2.59 (ddq, *J* = 15, 12, 2 Hz, 1H), 1.25 (t, *J* = 7 Hz, 3H), 1.14 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 171.72 (s), 171.34 (s), 140.18 (s), 136.98 (s), 133.92 (d), 129.59 (d, 2 × CH), 129.01 (d, 2 × CH), 116.27 (t), 70.10 (d), 61.58 (t), 61.20 (t), 48.70 (d), 47.23 (d), 38.21 (t), 14.11 (q) 13.94 (q); MS (CI/CH_4) *m*/*z* 367 (MH^+, 100), 321 (16), 293 (26), 225 (19). Anal. Calcd for $C_{18}H_{22}O_6S$: C, 59.00; H, 6.05; S, 8.75. Found: C, 58.73; H, 5.87; S, 8.45.

(1*β*,2α,3*β*)-1-Acetyl-2-methyl-4-methylene-3-(phenylsulfonyl)cyclopentane (6). Elution: EtOAc/petroleum ether 1:2. **6**: mp 137−139 °C; ^{1}H NMR δ 7.94−7.87 (m, 2H), 7.70−7.62 (m, 1H), 7.60−7.51 (m, 2H), 5.25 (t, *J* = 2 Hz, 1H), 5.11 (t, *J* = 1.5 Hz, 1H), 3.58 (dq, *J* = 8, 2 Hz, 1H), 2.85 (d quin, *J* = 10, 7 Hz, 1H), 2.58−2.41 (m, 2H), 2.31−2.15 (m, 1H), 2.12 (s, 3H), 1.02 (d, *J* = 7 Hz, 3H); ^{13}C NMR δ 207.03 (s), 141.70 (s), 137.17 (s), 133.66 (d), 129.49 (d, 2 × CH), 128.85 (d, 2 × CH), 115.35 (t), 74.69 (d), 58.65 (d), 38.11 (t), 37.92 (d), 28.94 (q), 19.73 (q); MS (CI/isobutane) *m*/*z* 296 ($M[H_2O]^+$, 44), 279 (MH^+, 100).

Ethyl (1α,1*β*,2α,3*β*)-3-(Phenylsulfonyl)-2-(ethoxycarbonyl)-1α-methyl-4-methylenecyclopentanecarboxylate (7). Elution: EtOAc/petroleum ether 1:4. **7**: ^{1}H NMR δ 7.95−7.89 (m, 2H), 7.69−7.62 (m, 1H), 7.59−7.51 (m, 2H), 5.33 (ddd, *J* = 3, 2, 1 Hz, 1H), 5.28 (ddd, *J* = 3, 1.5, 0.5 Hz, 1H), 4.56 (dqd, *J* = 8.5, 2, 0.5 Hz, 1H), 4.23, 4.14 (ABq of q, J_{gem} = 10.5 Hz, J_{vic} = 7 Hz, 2H), 4.04, 3.95 (ABq of q, J_{gem} = 10.5 Hz, J_{vic} = 7 Hz, 2H), 4.01 (d, *J* = 8.5 Hz, 1H), 2.76 (dqq, *J* = 14.5, 2, 0.8 Hz, 1H), 2.24 (d, *J* = 14 Hz, 1H), 1.27 (t, *J* = 7 Hz, 3H), 1.14 (t, *J* = 7 Hz, 3H), 1.00 (s, 3H); ^{13}C NMR δ 173.64 (s), 169.48 (s), 140.03 (s), 137.14 (s), 133.84 (d), 129.64 (d, 2 × CH), 128.94 (d, 2 × CH), 116.82 (t), 68.04 (d), 61.35 (t), 61.29 (t), 53.11 (d), 50.29 (s), 47.28 (t), 17.80 (q), 14.14 (q), 14.06 (q); MS (CI/CH_4) *m*/*z* 381 (MH^+, 100), 335 (21), 307 (15), 239 (39), 165 (15). Anal. Calcd for $C_{19}H_{24}O_6S$: C, 59.99; H, 6.36; S, 8.43. Found: C, 59.84; H, 6.26; S, 8.35.

Reactions of Methallyl Sulfone 8 with Ethyl Crotonate (9a) (Table 2).[24] To a stirred solution of LDA, prepared from 0.13 mL (0.99 mmol) of diisopropylamine and 0.63 mL of *n*-BuLi (0.95 mmol, 1.5 M solution in hexane) in 4 mL of THF, was added dropwise at −95 °C a solution of methallyl phenyl sulfone (**8**) (207 mg, 1.06 mmol) in 3.5 mL of THF. After 10 min, ethyl crotonate (86 mg, 0.75 mmol) in 2 mL of THF was added and stirring was continued for 20 min at the above temperature. Quenching (20% aqueous AcOH) and extraction (CH_2Cl_2) as before was followed by evaporation under reduced pressure. The diastereomeric ratio (**10a**/**11a**, 5.5:1) was established by the integration of the ^{1}H NMR spectrum of the crude mixture. Chromatographic purification on silica gel (EtOAc/petroleum ether 1:5) gave an inseparable mixture of **10a** and **11a** (83%). The above reaction was repeated under identical conditions by adding HMPA (0.4 mL in 0.2 mL of THF) to the reaction mixture (10 min after the addition of **8**), prior (5 min) to ethyl crotonate. After extraction with Et_2O, the integration of the ^{1}H NMR of the crude mixture showed a 1:1.5 ratio of **10a**:**11a**. Chromatographic purification gave 80% of the diastereomeric mixture.

Reactions of Methallyl Sulfone 8 with Ethyl Cinnamate (9b) (Table 2). The reaction of **8** with **9b** following the procedure and amounts as described for ethyl crotonate (**9a**) gave a sole product (TLC, ^{1}H NMR). Chromatographic purification (EtOAc/petroleum ether 1:5) gave **ethyl 5-methyl-3-phenyl-4-(phenylsulfonyl)-5-hexenoate (10b**; *anti*) (87%): mp 132−134 °C; ^{1}H NMR δ 7.52−7.41 (m, 3H), 7.34−7.25 (m, 2H), 7.09 (s, 5H), 5.30−5.25 (m, 2H), 4.05 (d, *J* = 9 Hz, 1H), 3.97 (td, *J* = 9.5, 3.5 Hz, 1H), 3.91 (ABq of q, J_{gem} = 10 Hz, J_{vic} = 7 Hz, 2H), 2.91 (dd, *J* = 16, 3.5 Hz, 1H), 2.61 (ddd, *J* = 16, 9.5, 1.5 Hz, 1H), 1.80 (t, *J* = 1 Hz, 3H), 1.03 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 170.86 (s), 140.18 (s), 139.09 (s), 136.63 (s), 132.70 (d), 128.55 (d, 4 × CH), 128.95 (d, 2 × CH), 128.16 (d, 2 × CH), 127.30 (d), 121.10 (t), 75.91 (d), 60.38 (t), 41.06 (d), 38.94 (t), 22.47 (q), 13.97 (q); MS (CI/NH_3) *m*/*z* 390 (MNH^+_4, 100), 373 (MH^+, 5). Anal. Calcd for $C_{21}H_{24}O_4S$: C, 67.71; H, 6.49. Found: C, 67.87; H, 6.46. The dominant conformer of **10b**, with *anti*-arranged methine hydrogens (*J* = 9 Hz), exhibits 3% and 2% NOE at -CH_2CO_2Et upon irradiation of the methyl and vinyl hydrogens, respectively.

(23) An excess of **1** was found necessary in order to prevent the formation of small amounts of a 1:2 donor/acceptor adduct originating from a Michael−Michael reaction.

(24) The reactions of **8** with **9a** were previously performed under different conditions; see ref 8 for configurational, spectroscopic, and analytical data of **10a** and **11a**.

Methallyl sulfone **8** was reacted with ethyl cinnamate (**9b**) in the presence of HMPA under the conditions and amounts given for ethyl crotonate. The reaction mixture was allowed to warm to −70 °C during 30 min. Workup as described earlier and ^{1}H NMR integration of the crude mixture showed a 1:4 ratio of **10b**:**11b**. Chromatographic purification (EtOAc/petroleum ether 1:5) gave by order of elution unreacted ethyl cinnamate (24%), **11b** (45%), and **10b** (10%).

11b (*syn*): mp 157−159 °C; ^{1}H NMR 7.88−7.83 (m, 2H), 7.64−7.57 (m, 1H), 7.55−7.46 (m, 2H), 7.25−7.13 (m, 5H), 4.72 (bs, 1H), 4.69 (ddd, J = 2, 1, 0.5 Hz, 1H), 4.15 (d, J = 11 Hz, 1H), 3.98 (td, J = 10, 4 Hz, 1H), 3.95 (ABq of q, J_{gem} = 10 Hz, J_{vic} = 7 Hz, 2H), 3.59 (dd, J = 15.5, 4 Hz, 1H), 2.97 (dd, J = 15.5, 10 Hz, 1H), 1.29 (dd, J = 1.5, 1 Hz, 3H), 1.07 (t, J = 7 Hz, 3H); ^{13}C NMR δ 171.06 (s), 140.35 (s), 138.99 (s), 137.61 (s), 133.40 (d), 129.12 (d, 2 × CH), 128.71 (d, 2 × CH), 128.56 (d, 2 × CH), 128.13 (d, 2 × CH), 127.02 (d), 121.38 (t), 75.16 (d), 60.20 (t), 41.61 (d), 40.31 (dd), 21.19 (q), 14.02 (q); MS (CI/NH_3) m/z 390 (MNH_4^+, 100), 373 (MH^+, 13); on irradiation of CH_3 protons, a 10% NOE was observed at the phenyl group; upon irradiation of the ortho proton of the $PhSO_2$ group a 2% NOE was exhibited at CH_2COOEt.

Reaction of Bromo Sulfone 1 with Diethyl Maleate. The reaction was performed under conditions shown for **2**−**7**, and then the mixture was allowed to warm from −95 to −50 °C during 1 h. Workup as described earlier and chromatographic purification (EtOAc/petroleum ether 1:3) gave by order of elution **12**, **13**, and **5**.

Ethyl 5-(bromomethyl)-3-(ethoxycarbonyl)-4-(phenylsulfonyl)-5-hexenoate (12, *syn*, 11%): mp 93−95 °C; ^{1}H NMR δ 7.87−7.80 (m, 2H), 7.70−7.62 (m, 1H), 7.58−7.49 (m, 2H), 5.62 (s, 1H), 5.60 (bs, 1H), 4.32 (d, J = 8 Hz, 1H), 4.24−4.15 (m, 4H), 3.75 (s, 2H), 3.50 (ddd, J = 10, 8, 4 Hz, 1H), 3.23 (dd, J = 17, 4 Hz, 1H), 3.12 (dd, J = 17, 10 Hz, 1H), 1.28 (t, J = 7 Hz, 3H), 1.25 (t, J = 7 Hz, 3H); ^{13}C NMR δ 171.15 (s), 170.79 (s), 137.29 (s), 136.60 (s), 134.21 (d), 129.52 (d, 2 × CH), 128.99 (d, 2 × CH), 124.06 (t), 67.21 (d), 61.63 (t), 60.90 (t), 42.57 (d), 35.33 (t), 34.28 (t), 14.16 (q), 13.96 (q); MS m/z 449, 447 (MH^+, 21, 19), 403, 401 (100, 95), 225 (95).

Ethyl (1α,2*β*,3*β*)-2-(ethoxycarbonyl)-4-methylene-3-(phenylsulfonyl)cyclopentanecarboxylate (13, 46%): mp 92−94 °C; ^{1}H NMR δ 7.89−7.83 (m, 2H), 7.68−7.61 (m, 1H), 7.58−7.49 (m, 2H), 5.12 (td, J = 2.5, 1.5 Hz, 1H), 4.85 (td, J = 2.5, 1.5 Hz, 1H), 4.35 (dq, J = 7, 1 Hz, 1H), 4.19, 4.05 (ABq of q, J_{gem} = 10.5 Hz, J_{vic} = 7 Hz, 2H), 4.12 (q, J = 7 Hz, 2H), 3.70 (ddd, J = 12, 11, 9 Hz, 1H), 3.55 (dd, J = 12, 7 Hz, 1H), 2.92 (ddtd, J = 17, 10.5, 2.5, 1.5 Hz, 1H), 2.39 (ddt, J = 17, 9, 2.5 Hz, 1H), 1.27 (t, J = 7 Hz, 3H), 1.23 (t, J = 7 Hz, 3H); ^{13}C NMR δ 173.51 (s), 168.78 (s), 140.70 (s), 137.81 (s), 133.94 (d), 129.67 (d, 2 × CH), 128.78 (d, 2 × CH), 116.65 (t), 72.35 (d), 61.45 (t), 61.02 (t), 49.53 (d), 42.88 (d), 33.83 (t), 14.12 (q), 13.97 (q); MS (CI/isobutane) m/z 384 ($[MH_2O]^+$, 45), 367 (MH^+, 100), 321 (15).

Reactions of Bromo Sulfone 1 with Cyclic Carbonyl Compounds. The general reaction conditions are as shown for acyclic acceptors. For reaction time and temperature, see Table 3.

Reaction with 2-Cyclohexen-1-one. Purification of the crude mixture of products by chromatography (EtOAc/petroleum ether 2:3) gave (by order of elution) a mixture of **15** + **16** (1:1, 22%) and then **(1*β*,6*β*,7*β*)-7-phenylsulfonyl-8-methylenebicyclo[4.3.0]nonan-2-one (14),** 48%, mp 140−142 °C; ^{1}H NMR δ 7.91−7.85 (m, 2H), 7.70−7.65 (m, 1H), 7.60−7.52 (m, 2H), 5.26 (dt, J = 3, 1.5 Hz, 1H), 4.98 (dt, J = 3, 1.5 Hz, 1H), 3.71 (dq, J = 5, 2 Hz, 1H), 3.18 (tt, J = 7.5, 5 Hz, 1H), 2.87 (td, J = 8, 5 Hz, 1H), 2.77 (ddt, J = 15.5, 5.5, 2 Hz, 1H), 2.44−2.32 (m, 2H), 2.32 (dd, J = 13, 6.5 Hz, 1H), 1.95−1.78 (m, 3H), 1.64 (dddd, J = 14, 10, 8, 2.5 Hz, 1H); ^{13}C NMR δ 210.01 (s), 141.51 (s), 137.25 (s), 133.81 (d), 129.46 (d, 2 × CH), 128.96 (d, 2 × CH), 116.48 (t), 72.86 (d), 50.55 (d), 43.34 (d), 39.32 (t), 34.39 (t), 27.12 (t), 22.72 (t); MS (CI/isobutane) m/z 291 (MH^+, 35), 149 (100). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.01; H, 6.27. Compounds **15** and **16** were characterized as an inseparable mixture of isomers with overlap of some ^{1}H NMR signals. **15**: ^{1}H NMR δ 7.94−7.48 (m, 5H), 5.65 (bs, 1H), 5.51 (s, 1H), 3.78 (d, J = 10.5 Hz, 1H), 3.70 (d, J = 7.5 Hz, 1H), 3.56 (d, J = 11 Hz, 1H), 3.02−1.44 (m, 9H). **16**: ^{1}H NMR δ 7.94−7.48 (m, 5H), 6.53 (s, 1H), 3.91 (s, 2H), 3.02−1.44 (m, 11H).

MS (**15** + **16**): CI (NH_3) m/z 390, 388 (MNH_4^+, 100, 85), 308 (87).

Reaction with 4,4-Dimethoxy-2,5-cyclohexadien-1-one. Purification by column chromatography (EtOAc/petroleum ether 2:3) gave **(1*β*,6*β*-5,5-dimethoxy-8-[((*Z*)-(phenylsulfonyl)methylene]bicyclo[4.3.0]non-3-en-2-one (17),** 65%, mp 87−89 °C; ^{1}H NMR δ 7.88−7.81 (m, 2H), 7.63−7.57 (m, 1H), 7.55−7.46 (m, 2H), 6.74 (dd, J = 10, 2 Hz, 1H), 6.22 (dddd, J = 3.5, 3, 2, 1.5 Hz, 1H), 6.00 (d, J = 10 Hz, 1H), 3.32 (s, 3H), 3.29 (s, 3H), 3.27 (dddtd, J = 19, 8, 2, 1.5, 0.5 Hz, 1H), 3.11 (dq, J = 18, 1.5 Hz, 1H), 2.96 (td, J = 11, 2.5 Hz, 1H), 2.91 (ddt, J = 9, 6.5, 1.5 Hz, 1H), 2.64 (ddt, J = 18, 8, 2.5 Hz, 1H), 2.50 (ddt, J = 19, 11, 2.5 Hz, 1H); ^{13}C NMR δ 198.31 (s), 159.44 (s), 146.80(d), 141.57 (s), 133.07 (d), 129.65 (d), 129.02 (d, 2 × CH), 126.90 (d, 2 × CH), 123.02 (d), 97.49 (s), 49.36 (q), 48.08 (q), 46.00 (d), 45.65 (d), 38.29 (dd), 31.37 (dd); MS (CI/NH_3) m/z 366 (MNH_4^+, 35), 334 (95), 317 (100).

Reaction with 5,6-Dihydro-2*H*-pyran-2-one. Chromatographic purification of the crude mixture (EtOAc/petroleum ether 1:1) gave by order of elution **19** and then **18**.

(4aα,5α,7a*β*)-6-Methylene-5-(phenylsulfonyl)hexahydrocyclopenta[*c*]pyran-1-one (18), 66%: mp 126−128 °C; ^{1}H NMR δ 7.92−7.86 (m, 2H), 7.72−7.65 (m, 1H), 7.62−7.53 (m, 2H), 5.25 (dt, J = 3, 2 Hz, 1H), 4.81 (dt, J = 3, 2Hz, 1H), 4.32 (ddd, J = 11.5, 4.5, 3.5 Hz, 1H), 4.24 (ddd, J = 11.5, 11, 2.5 Hz, 1H), 3.71 (dq, J = 4, 1.5 Hz, 1H), 3.35 (tdd, J = 9.5, 7, 4 Hz, 1H), 3.16 (td, J = 9, 4.5 Hz, 1H), 2.88, (ddt, J = 16.5, 4.5, 1.5 Hz, 1H), 2.81 (ddtd, J = 16.5, 9, 2.5, 1.5 Hz, 1H), 2.07 (dddd, J = 14.5, 7, 4.5, 3.5 Hz, 1H), 1.65 (dddd, J = 14.5, 11, 10, 4.5 Hz, 1H); ^{13}C NMR δ 171.95 (s), 140.60 (s), 136.50 (s), 134.11 (d), 129.33 (d, 2 × CH), 129.11 (d, 2 × CH), 117.02 (t), 75.44 (d), 66.80 (t), 41.83 (d), 37.80 (t), 35.55 (t), 28.48 (t); MS (CI/NH_3) m/z 310 (MNH_4^+, 100), 293 (MH^+, 56), 151 (7). Anal. Calcd for $C_{15}H_{16}O_4S$: C, 61.63; H, 5.51. Found: C, 61.78; H, 5.49.

(3′*S,4*S**)-4-[2′-(Bromomethyl)-3′-(phenylsulfonyl)-1′-propen-3′-yl]tetrahydro-2*H*-pyran-2-one (19)**, 12%, colorless oil: ^{1}H NMR δ 7.88−7.79 (m, 2H), 7.73−7.65 (m, 1H), 7.65−7.52 (m, 2H), 5.65 (bs, 1H), 5.41 (s, 1H), 4.44 (ddd, J = 11.5, 4.5, 3.5 Hz, 1H), 4.23 (td, J = 11, 3.5 Hz, 1H), 3.77 (dd, J = 11, 1 Hz, 1H), 3.72 (d, J = 9 Hz, 1H), 3.44 (dd, J = 11, 1 Hz, 1H), 3.27 (ddd, J = 17, 5, 2 Hz, 1H), 2.80 (tddd, J = 11, 9, 5.5, 4.5 Hz, 1H), 2.65 (dd, J = 17.5, 10.5 Hz, 1H), 2.14 (ddtd, J = 13.5, 7, 3.5, 2 Hz, 1H), 1.82 (dtd, J = 13.5, 11, 5 Hz, 1H); ^{13}C NMR δ 169.09 (s), 137.60 (s), 136.58 (s), 134.34 (d), 129.45 (d, 2 × CH), 129.23 (d, 2 × CH), 124.15 (t), 71.41 (d), 67.89 (t), 36.48 (t), 35.78 (dd), 32.25 (d), 27.15 (t); MS (CI/NH_3) m/z 392 (MNH_4^+, 100), 374 (MH^+, 0.5), 346 (6), 312 (8).

Reaction with 2(5*H*)-Furanone. Chromatographic purification of the crude mixture (EtOAc/petroleum ether 1:1) gave by order of elution **22**, **20**, and **21**.

(3a*β*,6a*β*,4*β*)-5-Methylene-4-(phenylsulfonyl)hexahydrocyclopenta[*c*]furan-1-one (20), 69%: mp 134−136 °C; ^{1}H NMR δ 7.90−7.85 (m, 2H), 7.73−7.66 (m, 1H), 7.62−7.54 (m, 2H), 5.20 (dtd, J = 3, 1.5, 1 Hz, 1H), 4.70 (dtd, J = 3, 1.5, 1Hz, 1H), 4.53 (dd, J = 10, 7 Hz, 1H), 4.09 (dd, J = 10, 3 Hz, 1H), 3.83 (qd, J = 3, 1 Hz, 1H), 3.72 (tt, J = 8, 3 Hz, 1H), 3.17 (td, J = 9, 2 Hz, 1H), 2.90 (dddd, J = 16, 9.5, 3, 2 Hz, 1H), 2.70 (ddd, J = 16, 2, 1 Hz, 1H); ^{13}C NMR δ 177.93 (s), 140.69 (s), 136.11 (s), 134.25 (d), 129.37 (d, 2 × CH), 129.14 (d, 2 × CH), 117.65 (t), 75.72 (d), 71.76 (t), 43.34 (d), 40.89 (d), 36.12 (t); MS (CI/NH_3) m/z 575 ($M_2NH_4^+$, 15), 296 (MNH_4^+, 100).

(3a*β*,6a*β*)-5-Methyl-4-(phenylsulfonyl)-3,3a,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-1-one (21), 7%: mp 102−104 °C; ^{1}H NMR δ 7.90−7.77 (m, 2H), 7.69−7.47 (m, 3H), 4.76 (dd, J = 11, 3 Hz, 1H), 4.42 (dd, J = 11, 7.5 Hz, 1H), 3.96−3.82 (m, 1H), 3.13 (ddd, J = 8, 7, 5 Hz, 1H), 2.93 (bd, J = 6 Hz, 2H), 2.15 (bs, 3H); ^{13}C NMR δ 178.87 (s), 156.47 (s), 141.58 (s), 134.49 (s), 133.60 (d), 129.44 (d, 2 × CH), 126.88 (d, 2 × CH), 70.97 (dd), 48.29 (d), 43.11 (t), 39.65 (d), 15.50 (q); MS (CI/NH_3) m/z 296 (MNH_4^+).

(4*R,3′*R**)-4-[2′-(Bromomethyl)-3′(phenylsulfonyl)-1′-propen-3′-yl]dihydro-2*H*-furan-2-one (22),** 8%: ^{1}H NMR

δ 7.85−7.79 (m, 2H), 7.76−7.68 (m, 1H), 7.63−7.53 (m, 2H), 5.62 (bs, 1H), 5.17 (s, 1H), 4.33 (dd, J = 10, 8 Hz, 1H), 4.07 (t, J = 9 Hz, 1H), 3.90 (d, J = 11 Hz, 1H), 4.87 (d, J = 11 Hz, 1H), 3.64 (dd, J = 11, 1 Hz, 1H), 3.16 (tdt, J = 11, 10, 8 Hz, 1H), 2.91 (dd, J = 18, 8 Hz, 1H), 2.65 (dd, J = 18, 11 Hz, 1H); ^{13}C NMR δ 175.37 (s), 137.10 (s), 136.24 (s), 134.72 (d), 129.61 (d, 2 × CH), 129.39 (d, 2 × CH), 123.45 (t), 69.97 (t), 69.56 (d), 36.29 (t), 34.91 (d), 34.11 (t); MS (CI/NH_3) m/z 376 (MNH_4^+, 100), 359 (MH^+, 3), 332 (15), 298 (48).

Reactions of Methallyl Sulfone 8 with Cyclic Carbonyl Compounds. The conditions and amounts were identical with those used in reactions of **8** with ethyl crotonate, in the absence or presence of HMPA. The diastereomeric ratio was established by integration of the vinylic protons in the crude mixture (Table 4).

Reactions with 2-Cyclohexen-1-one. In the absence of HMPA, chromatographic purification (EtOAc/petroleum ether 2:3) gave by order of elution **23a** (9%), **23b** (9%), and **24** (7%). In the presence of HMPA, a similar purification gave **23a** (61%) and **23b** (20%).

(3*S,3′*R**)-3-[2′-Methyl-3′-(phenylsulfonyl)-1′-propen-3′-yl]cyclohexan-1-one (23a)**: mp 94−96 °C; ^{1}H NMR δ 7.86−7.79 (m, 2H), 7.66−7.58 (m, 1H), 7.55−7.47 (m, 2H), 4.96−4.91 (m, 1H), 4.86 (s, 1H), 3.57 (d, J = 9 Hz, 1H), 2.79−2.55 (m, 2H), 2.47 (ddt, J = 14, 4, 2 Hz, 1H), 2.41 (ddt, J = 14, 4, 2 Hz, 1H), 2.32 (ddd, J = 7, 6, 1 Hz, 1H), 2.22−2.12 (m, 1H), 2.11 (ddd, J = 14, 11.5, 1 Hz, 1H), 1.85−1.67 (m, 2H), 1.58 (bs, 3H); ^{13}C NMR δ 209.28 (s), 138.83 (s), 136.64 (s), 133.34 (d), 128.62 (d, 2 × CH), 128.55 (d, 2 × CH), 121.00 (t), 76.03 (d), 45.32 (dd), 41.09 (t), 37.53 (d), 29.82 (dd), 24.57 (t), 21.15 (q); MS (CI/isobutane) m/z 310 ($[M(H_2O)]^+$, 20), 293 (MH^+, 100), 151 (98).

(3*S,3′*S**)-3-[2′-Methyl-3′-(phenylsulfonyl)-1′-propen-3′-yl]cyclohexan-1-one (23b)**: mp 150−152 °C; ^{1}H NMR δ 7.87−7.80 (m, 2H), 7.66−7.59 (m, 1H), 7.56−7.47 (m, 2H), 5.03 (bs, 1H), 4.93 (s, 1H), 3.49 (d, J = 8 Hz, 1H), 2.88 (ddt, J = 14, 4, 2 Hz, 1H), 2.71 (dddd, J = 15, 11.5, 7.5, 3.5 Hz, 1H), 2.43 (dddd, J = 14, 6, 3, 2 Hz, 1H), 2.37 (ddd, J = 14, 12, 1 Hz, 1H), 2.26 (dddd, J = 14, 8, 7, 2 Hz, 1H), 2.19−2.20 (m, 1H), 2.08 (ddq, J = 9, 6.5, 3 Hz, 1H), 1.70−1.65 (m, 1H), 1.66 (bs, 3H), 1.57 (dddt, J = 16, 13, 3, 2 Hz, 1H); ^{13}C NMR δ 209.20 (s), 138.95 (s), 136.58 (s), 133.51 (d), 128.77 (d, 4 × CH), 121.27 (t), 76.12 (d), 46.45 (dd), 41.03 (t), 37.54 (d), 28.70 (t), 24.60 (t), 22.06 (q); MS (CI/isobutane) m/z 310 ($[M(H_2O)]^+$, 3), 293 (MH^+, 55), 151 (100).

3-[(*E*)-(2′-Methyl-1′-(phenylsulfonyl)-1′-propen-3′-yl]cyclohexan-1-one (24), colorless oil; ^{1}H NMR δ 7.95−7.85 (m, 2H), 7.66−7.50 (m, 3H), 6.19 (q, J = 1 Hz, 1H), 2.43−2.26 (m, 2H), 2.21 (bdd, J = 15, 7 Hz, 1H), 2.14 (bd, J = 8 Hz, 1H), 2.10 (bs, 3H), 2.08−2.00 (m, 2H), 1.94 (td, J = 11, 1Hz, 1H), 1.82 (bd, J = 14 Hz, 1H), 1.70−1.54 (m, 3H); ^{13}C NMR δ 209.82 (s), 154.25 (s), 142.35 (s), 133.13 (d), 129.18 (d, 2 × CH), 128.11 (d), 127.08 (d, 2 × CH), 47.57 (t), 47.41 (t), 41.16 (t), 36.65 (d), 30.87 (dd), 24.79 (dd), 17.65 (q); MS (CI/NH_3) m/z 310 (MNH_4^+, 100).

Reactions with 5,6-Dihydro-2*H*-pyran-2-one. In absence of HMPA, chromatographic purification of the crude product (EtOAc/petroleum ether 1:1) gave by order of elution **25a** (63%) and **25b** (22%). Similar purification of the crude product obtained in presence of HMPA gave **25a** (71%) and **25b** (12%).

(4*S,1′*R**)-4-[2′-Methyl-3′-(phenylsulfonyl)-1′-propen-3′-yl]tetrahydro-2*H*-pyran-2-one (25a),** colorless oil: ^{1}H NMR δ 7.86−7.78 (m, 2H), 7.69−7.60 (m, 1H), 7.57−7.48 (m, 2H), 4.95 (bs, 1H), 4.83 (s, 1H), 4.53 (ddd, J = 11.5, 5.5, 3.5 Hz, 1H), 4.36 (td, J = 11.5, 3.5 Hz, 1H), 3.51 (d, J = 10 Hz, 1H), 2.91 (dtdd, J = 11, 10, 6, 4 Hz, 1H), 2.74 (dqd, J = 16, 4, 2 Hz, 1H), 2.68 (ddd, J = 18, 6.5, 2 Hz, 1H), 2.23 (dd, J = 18, 10 Hz, 1H), 2.04 (dtd, J = 16, 11, 5 Hz, 1H), 1.60 (bs, 3H); ^{13}C NMR δ 169.55 (s), 138.27 (s), 136.28 (s), 133.85 (d), 128.87 (d, 4 × CH), 121.93 (t), 75.86 (t), 68.21 (t), 34.40 (dd), 30.98 (d), 28.10 (dd), 20.77 (q); MS (CI/isobutane) m/z 312 ($[M(H_2O)]^+$, 98), 295 (MH^+, 100).

(4*S,1′*S**)-4-[2′-Methyl-3′-(phenylsulfonyl)-1′-propen-3′yl]tetrahydro-2*H*-pyran-2-one (25b),** colorless oil: ^{1}H NMR δ 7.87−7.79 (m, 2H), 7.68−7.61 (m, 1H), 7.57−7.48 (m, 2H), 5.02 (bs, 1H), 4.89 (s, 1H), 4.44 (ddd, J = 12, 5, 4 Hz, 1H), 4.28 (td, J = 11, 4 Hz, 1H), 3.53 (d, J = 9 Hz, 1H), 3.23 (ddd, J = 16, 6, 2 Hz, 1H), 2.91 (tddd, J = 11, 9, 6, 4 Hz, 1H), 2.68 (dd, J = 18, 11 Hz, 1H), 2.05 (dqd, J = 15, 4, 2 Hz, 1H), 1.72 (dtd, J = 16, 11, 5 Hz, 1H), 1.64 (bs, 3H); ^{13}C NMR δ 169.26 (s), 138.17 (s), 136.12 (s), 133.70 (d), 128.76 (d, 2 × CH), 128.66 (d, 2 × CH), 121.79 (t), 75.49 (d), 67.84 (t), 35.42 (t), 30.95 (d), 26.78 (t), 21.31 (q); MS (CI/isobutane) m/z 312 ($[M(H_2O)]^+$, 90), 295 (MH^+, 100).

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Supporting Information Available: ^{13}C NMR spectra (14 pages). This material is available in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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