# Synthesis of Nitrocyclopentanes via a 3 + 2 Strategy

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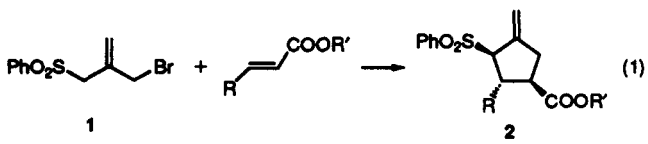
*Received June 22, 1993*•

Reactions of 1-(phenylsulfonyl)-2-methylene-3-bromopropane (1) with various nitroolefins have been investigated with the purpose of devising a tandem [3 + 2]-annulation leading to nitro-substituted derivatives of methylenecyclopentanes. The conjugate addition step occurred readily affording **4a–e** (*syn*) and **5a–e** (*anti*) adducts. The *anti*-adducts cyclized further in the presence of HMPA to give stereoisomeric methylenecyclopentane derivatives **6a–f** and **7a–f**. At higher reaction temperature, partial ring closure of **4a–d**-*syn* isomers to give *cis*-2,3-disubstituted cyclopentanes **8a–d** could also be achieved. Base-induced equilibration provided in a one-vessel operation, starting from 1 and 1-nitrobutene (**3b**), the methylenecyclopentane **6b** with three stereogenic centers. The difference in the stereochemical outcome of the Michael addition step with nitroolefins, as compared with reactions in which $\alpha,\beta$-unsaturated esters served as acceptors for 1, may be attributed to the better chelating ability of the lithium counterion in the latter reactions, based upon the results obtained in conjugate additions of methallyl sulfone **9** with 1-nitropropene and crotonic ester. The presence of HPMA strongly influenced the stereochemical outcome of reactions of **9** with ethyl crotonate but not with 1-nitropropene as the Michael acceptor. Reactions of 1 with 1-nitro-2-arylethenes afforded *trans–trans*-substituted methylenecyclopentanes as the major products. The reaction of 1 with 1-nitrocyclohexene afforded the *cis*-hydrindane derivative **21**. The described reactions provide the first example of intramolecular trapping of nitronates resulting from Michael additions by alkyl/allyl halides.

## Introduction

The considerable importance of cyclopentanoid natural products has led in recent years to the development of a great number of new strategies for the construction of cyclopentanes.[2] While most of the cyclization methodologies have involved one-bond formation, the effectiveness of cyclopentation has been increased by direct formation of rings from two moieties, like in [3 + 2] annulation processes.[2,3] Such methodology depends in great measure on the ready availability of the two carbon fragments and the possibility to obtain a broad range of substituted cyclopentanes as synthetic intermediates for further transformations. Our interest in tandem annulations[4] has led to the preparation and utilization of a 1,3-dipolar reagent, 1-(phenylsulfonyl)-2-methylene-3-bromopropane (1),[5] an equivalent of trimethylenemethane, which combines a carbanion center stabilized by an allylic sulfone group with the allylic halide as the electrophile, and is able to undergo intermolecular carbon–carbon-forming reactions without self-destruction. We have reported preliminary results of reactions of 1 with $\alpha,\beta$-unsaturated esters leading to stereohomogeneous methylenecyclopentanes **2** by a one-pot Michael addition–alkylation sequence (eq 1).[5]




1 2 (1)

In the present paper we describe the outcome of reactions of reagent 1 with nitroolefins, which afford nitro-substituted cyclopentanes by a similar scheme. Our interest in such a scheme was motivated by the versatility of the nitro group[6] which could provide a tool for further interesting transformations of the resulting cyclic products. However, a serious challenge was involved in this scheme: nitroolefins, while excellent Michael acceptors, afford nitronate adducts of very poor reactivity for further C-alkylation or allylation because of preferential oxygen attack on the halide.[7] In intermolecular reactions, double deprotonation of primary nitroalkanes was found to improve the ratio of C/N alkylations while allylations were previously achieved solely via conversion of lithiated nitroalkanes into lithium–copper complexes used in 2-fold excess.[8] We are not aware of previous attempts to carry out inter- or intramolecular C-alkylations or allylations by direct halide trapping of nitronates resulting from Michael reactions; however, the trapping of such adducts by aldehydes, involving the well-known nitroaldol ("Henry") reaction, has been recently reported.[9]

Notwithstanding these difficulties, it was reasoned that the intramolecularity of the allylation step in the projected scheme would be of help in achieving ring closure leading to nitro-substituted methylenecyclopentanes.

## Results and Discussion

Our initial experiments were conducted with aliphatic nitroolefins, prepared best via the nitroaldol reaction

• Abstract published in *Advance ACS Abstracts*, October 1, 1993.

(1) Stereochemistry 84. For paper 83 see Naidorf, S.; Hassner, A. *J. Org. Chem.*, in press.

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

(3) See Trost, B. M.; Seoane, P.; Mignani, S.; Acamoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487 and refs therein.

(4) Ghera, E.; Maurya, R.; Ben-David, Y. *J. Org. Chem.* **1988**, *53*, 1912.

(5) Ghera, E.; Yechezkel, T.; Hassner, A. *Tetrahedron Lett.* **1990**, *31*, 3653.

(6) Seebach, D.; Colvin, E. W.; Lehr, F.; Weller, T. Chimia **1977**, *33*, 1.

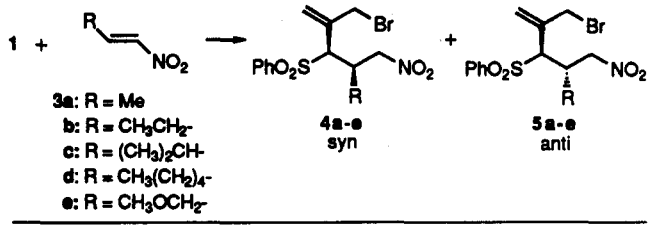
(7) See e.g. Wade, P. A.; Morrow, S. D.; Hardinger, S. A. *J. Org. Chem.* **1982**, *47*, 365 and refs cited therein.

(8) Seebach, D.; Lehr, F. *Helv. Chim. Acta* **1979**, *62*, 2239.

(9) Posner, G. H.; Crouch, R. D. *Tetrahedron* **1990**, *46*, 7509.

0022-3263/93/1958-6716$04.00/0 

**Table I. Michael Addition of 1 with Nitroolefins (−100 °C, 5 min)**




| entry | nitroolefin | base | *syn*/*anti* (ratio) | total yield |
|---|---|---|---|---|
| 1 | **3a** | LDA | **4a**/**5a** (1:0.8) | 69 |
| 2 | **3b** | LDA | **4b**/**5b** (1:1.5) | 75 |
| 3 | **3b** | LTMP | **4b**/**5b** (1:1.5) | 75 |
| 4 | **3b** | LTMP–HBr | **4b**/**5b** (1:1) | 66 |
| 5 | **3c** | LDA | **4c**/**5c** (1:2) | 73[a] |
| 6 | **3d** | LDA | **4d**/**5d** (1:1.5) | 72 |
| 7 | **3e** | LDA | **4e**/**5e** (1:1.3) | 61 |

[a] Cyclized product (**6c**, 20%) was also formed and is included in the yield.

followed by a somewhat modified olefination.[10] Low-temperature deprotonation of **1** with lithium diisopropylamide in tetrahydrofuran (THF), followed by addition of the nitroolefin, resulted in the immediate formation of the Michael adduct (as evidenced by TLC). The subsequent intramolecular allylation, however, proved to be sluggish and, upon warming, the cyclization competes with polymerization of the open-chain adduct. Attempts to utilize the previously developed methods for C-alkylation and allylation of nitronates[8] were unsuccessful. The addition of a second molar equivalent of base, for double deprotonation of the Michael adduct, led to increased polymerization, while conversion to a Cu–Li complex[8] (which cannot be used in excess due to the presence of the allyl bromide moiety and the intramolecularity of the reaction) did not improve substantially the cyclization results.

We then investigated the two-stage process in more detail with the hope that isolation of the open-chain Michael adducts and determination of their stereochemistry could be helpful in overcoming some of the setbacks of the ring closure. Hence, fast quenching of the reaction at −100 °C (4–5 min) provided good yields of a mixture of *syn* (**4**) and *anti* (**5**) diastereomeric Michael adducts (Table I),[11] with stereochemical assignments based on spectroscopic data. Examination of $^1$H NMR spectra showed, for both diastereomers, the preference for the lowest energy conformers as revealed by the coupling constants of the α-phenylsulfonyl methine protons (e.g., δ 3.94, $J$ = 9 Hz for **4a** and δ 3.84, $J$ = 8 Hz for **5a**) and, accordingly, NOE data (Figure 1) enabled the assignment of *syn* and *anti* stereochemistry for **4a** and **5a**, respectively.

Stereomeric assignments for other products in Table I were established analogously with **4**/**5** ratios calculated from integrated $^1$H NMR spectra of crude products. In a single case (entry 5) partial cyclization to **6c** occurred under the given conditions.

Utilization of lithium tetramethylpiperidide (LTMP) (entry 3) or LTMP–HBr (entry 4) did not improve the stereoselectivity of the Michael additions. Hence, while

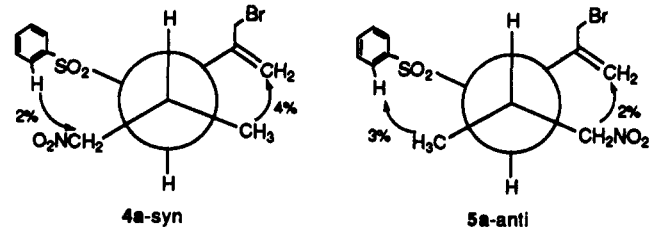
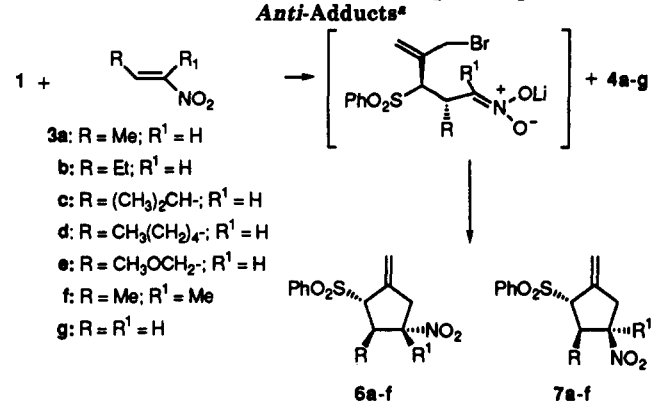



**Figure 1.**

**Table II. Reactions of 1 with 3 Leading to Ring Closure of *Anti*-Adducts[a]**




| | products, yield (%) | | |
|---|---|---|---|
| nitroolefin | **4** | **6** | **7** |
| **3a** | 46 | 12 | 19 |
| **3b** | 34 | 15 | 26 |
| **3c** | 25 | 55 | – |
| **3d** | 24 | 25 | 13 |
| **3e** | 27 | 29 | 7 |
| **3f** | 4 | 40 | 11 |
| **3g** | 80[b] | – | – |

[a] In the presence of HMPA, −78 °C. [b] No *syn*- and *anti*-isomers are involved; for cyclization see Table III.

our previous results of cyclopentanation with α,β-unsaturated esters as acceptors (eq 1) implied complete stereoselection in the Michael addition step, the stereochemical outcome of analogous reactions with nitroolefins did not result in a preferential formation of the *anti*-isomers, as precursors of 2,3-trans-disubstituted 1-methylenecyclopentanes.

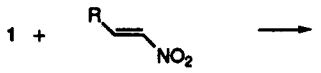
With these results at hand, we attempted next to effect the Michael addition and subsequent cyclization in one operation, by reacting bromo sulfone **1** with various nitroolefins under the above conditions and then adding HMPA as cosolvent (THF/HMPA 3:1)[12] with subsequent rise in temperature to −78 °C. Quenching the mixture after 2 h resulted in the selective cyclization of the *anti*-adducts to afford **6a-f** and **7a-f** (Table II), whereas the *syn*-diastereomers **4a-f** and the nitroethylene adduct **4g** failed to undergo ring closure and were isolated as open-chain adducts. Apart from the intrinsic difficulty of nitronate allylation at carbon, the cyclization of *syn*- as compared to *anti*-diastereomers should occur more reluctantly, in view of the resulting hindrance in *cis*-2,3-disubstituted 1-methylenecyclopentanes. The stereochemical assignments for cyclopentanes, as depicted, were based on $^1$H NMR evidence and NOE measurements. For instance, **6b** showed a 7% enhancement of the α-nitro proton at C-4 when the ethyl group was irradiated, whereas

(10) Milton, J.; McMurry, J. E. *J. Org. Chem.* **1975**, *40*, 2138. See also Experimental Section.

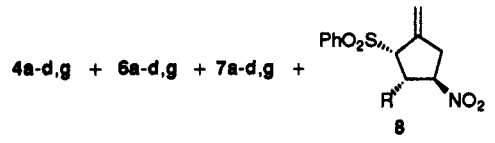
(11) *syn* and *anti* designations are based on the extended form including both anion-stabilizing groups; see Oare, D. A.; Heathcock, C. H. In *Topics in Stereochemistry*; Eliel, E. L., Wilen, S. H., Eds.; Wiley: New York, 1989; Vol. 19, p 227.

(12) Addition of HMPA prior to nitroolefin led to self-cyclization of **1** to 2-(phenylsulfonyl)-1-methylenecyclopropane as the major product. See also Najera, K.; Sansano, J. M. *Tetrahedron* **1992**, *24*, 5179.

**Table III. Reaction of 1 with 3 Leading to Ring Closure of *Anti*- and *Syn*-adducts[a]**



3a: R = Me
b: R = $CH_3CH_2$-
c: R = $(CH_3)_2CH$-
d: R = $CH_3(CH_2)_4$-
g: R = H



| | products, yields (%) | | | |
|---|---|---|---|---|
| nitroolefin | 4 | 6 | 7 | 8 |
| 3a | 25 | 24 | 18 | 16 |
| 3b | 18 | 24 | 21 | 17 |
| 3c | 4 | 33 | - | 22 |
| 3d | 15 | 40 | - | 12 |
| 3g | 14 | 24 | 25 | - |

[a] In the presence of HMPA, −78 °C for 1 h and then −40 °C for 1.5 h.

in **7b** a 9% enhancement was observed between the *cis* C-3 and C-4 protons, as compared with only 2% enhancement of the above *trans* protons in **6b**.

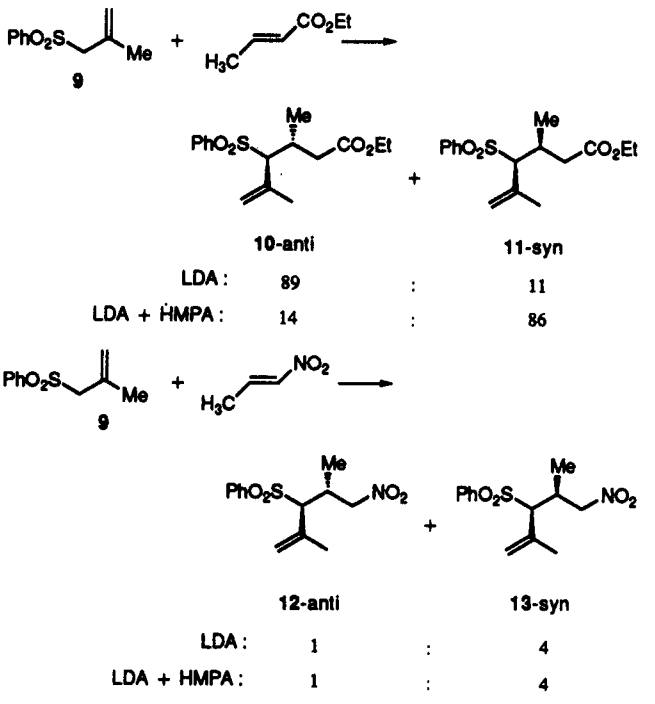
It is possible that the lack of stereoselectivity in the cyclization step, in which stereomers **6** and **7** are formed, is due to the presence of HMPA which disrupts chelation between the Li counterion and the oxygens of sulfone and nitro groups. Such chelation occurred effectively in the absence of HMPA in the ring-closure step involving $\alpha,\beta$-unsaturated esters (eq 1) which was indeed characterized by complete stereoselectivity. The cyclization to a single methylenecyclopentane derivative **6c** is probably due to the bulkiness of the isopropyl group. Interestingly, the conjugate addition of **1** involving 1-methylnitropropene as the acceptor afforded better stereoselectivity to give only 4% of the *syn*-adduct **4f** and the presence of an $\alpha$-nitromethyl substituent did not prevent ring closure of the *anti*-isomer to **6f** and **7f**. We are not aware of previous successful alkylations or allylations of secondary $\alpha$-nitro carbanions.[13]

Next, the reaction temperature was increased from −78 °C to −40 °C in a partly successful attempt to also cyclize the *syn*-diastereomer to **8** (Table III). Further increase of temperature produced partial polymerization of the open-chain adducts and therefore was not useful. The nitroethylene adduct **4g** underwent cyclization to **6g** and **7g**. The preferential *trans* arrangement of the nitro group in **8a–d** was established by $^1H$ NMR ($J_{3,4}$ = 10 Hz) while a 10% NOE between C-2 and C-3 protons confirmed the *cis*-substitution at these centers.

We found that base-induced equilibration of **6–8** can be achieved in the same pot, subsequent to the cyclization, leading to stereohomogeneous *trans–trans* trisubstituted methylenecyclopentanes thus obtained in one operation from bromo sulfone **1** and nitroolefins. For instance, addition of BuLi (0.6 equiv) at −78 °C to the reaction mixture obtained as in Table III from **1** and 1-nitrobutene (**2b**) afforded a 45% yield of stereohomogeneous **6b** along with 10% of open chain *syn* adduct **4b**.

(13) For an unsuccessful attempt, see Brändly, V.; Eger, M.; Seebach, D. *Chem. Ber.* **1986**, *119*, 575.

**Scheme I**



| | | | |
|---|---|---|---|
| LDA: | 89 | : | 11 |
| LDA + HMPA: | 14 | : | 86 |

| | | | |
|---|---|---|---|
| LDA: | 1 | : | 4 |
| LDA + HMPA: | 1 | : | 4 |

The stereochemical outcome of the conjugate addition step to nitroolefins (Table I) is thus remarkably different from the high stereoselectivity achieved with unsaturated esters as acceptors.[5] A retro-Michael–Michael process being improbable under the given reaction conditions,[14] we assume that the reactions are kinetically controlled, the transition state being dependent on the ability of the sulfone and acceptor oxygen atoms to chelate with the lithium ion.[15] As indicated, the additions of the allylic $\alpha$-sulfonyl carbanion to nitroolefins occur very rapidly, whereas in reactions of **1** with $\alpha,\beta$-unsaturated esters (eq 1) open-chain adducts could not be detected, suggesting that the ring closure is the faster step.[5] In order to compare the relative addition rates, we have reacted the bromine-devoid analog of **1**, namely methallyl sulfone **9**, with ethyl crotonate and nitropropene as the respective acceptors (Scheme I) under the same conditions. In both cases the addition proceeded with high regioselectivity via the $\alpha$-sulfonyl terminus.[16,17] The addition of **9** to **3a** was very rapid (<5 min), while the completion of reaction with ethyl crotonate required 1–1.5 h. A contrasting diastereomeric ratio was obtained: with ethyl crotonate the *anti*-diastereomer **10** was the major product (89:11 *anti/syn* ratio) whereas with nitropropene the *syn*-isomer **13** was preferentially formed (1:4 *anti/syn* ratio).

These contrasting stereochemical results, which depend on the electrophilic group of the acceptor, prompted us to perform analogous reactions of **9** in the presence of HMPA which, by solvating the lithium ion should prevent the complexation of the latter with both donor and acceptor. With ethyl crotonate as acceptor, a strikingly different diastereomeric ratio was obtained under otherwise iden-

(14) See e.g., Trost, B. M., Chan, D. M. T. *J. Am. Chem. Soc.* **1982**, *104*, 3733 and ref 11.
(15) Binns, M. R.; Haynes, R. K., Katsifis, A. G. Schober, P. A.; Vonwiller, S. C. *J. Org. Chem.* **1989**, *54*, 1960.
(16) Ghera, E.; Ben-Yaakov, E.; Yechezkel, T.; Hassner, A. *Tetrahedron Lett.* **1992**, *33*, 2741. The *syn* and *anti* designations in the above paper were based on the longest extended form instead of using the rules given in ref 10.
(17) Kraus, G. A.; Frazer, K. *Synth. Commun.* **1978**, *8*, 483.

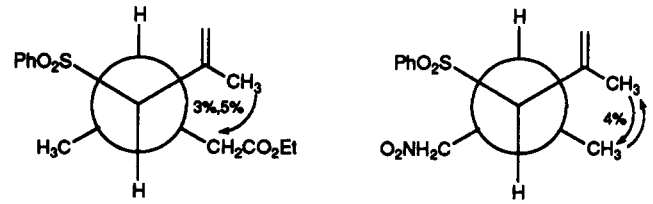
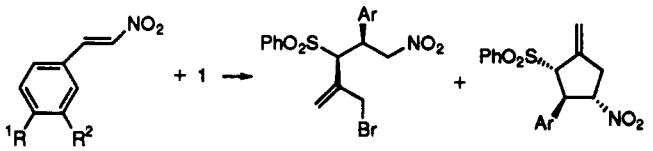



**Figure 2.**

**Table IV. Reactions of 1 with 1-Nitro-2-arylethenes**

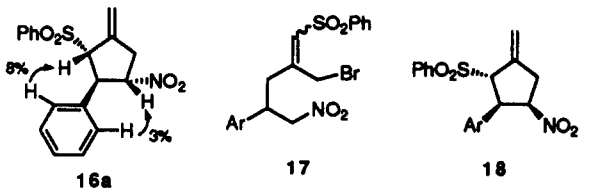



| | reaction time (min) | 15 (yield, %) | 16 (yield, %) |
|---|---|---|---|
| **14a**: $R^1 = R^2 = H$ | 105 | 13 | 44 |
| **14b**: $R^1 = OMe; R^2 = H$ | 90 | 19 | 54 |
| **14c**: $R^1 = R^2 = OMe$ | 105 | 18 | 42 |
| **14d**: $R^1 = Cl; R^2 = H$ | 105 | 14 | 42 |
| **14e**: $R^1 = Me; R^2 = H$ | 105 | 20 | 50 |
| **14f**: $R^1R^2 = OCH_2O$ | 120 | 20 | 40 |

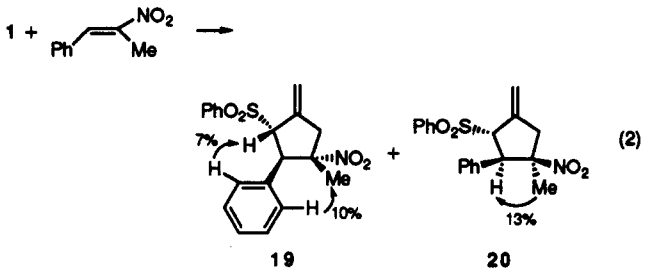
tical reaction conditions to give mainly the *syn*-product while with nitropropene (**3a**) the presence of HMPA did not affect the **12**/**13** ratio (see Scheme I). The influence of chelation, favoring the formation of the *anti*-diastereomer, is thus strongly evidenced in the reaction of **9** with ethyl crotonate, whereas with nitropropene this influence seems negligible. We may tentatively assume that the chelation ability decreases for nitroolefins due to a lower energy transition state leading to a very rapid Michael addition. Accordingly, the possibility to slow down the rate of conjugate addition may result in a more pronounced chelation and thus increase the formation of the desired *anti*-diastereomer. An attempt to achieve this goal was only partly successful by using hexane as cosolvent (THF/hexane 1:1) in the reaction of bromo sulfone **1** with nitrobutene (**3b**) under otherwise identical conditions to give a 2.5:1 **5b**-*anti*/**4b**-*syn* ratio (68% total yield) instead of the 1.5:1 ratio (Table I), in absence of hexane. When the above reaction was performed under conditions enabling ring closure of the *anti*-diastereomer (Table II), somewhat increased yields of **6b** (19%) and **7b** (29%), along with 22% of open-chain *syn*-diastereomer **4b** were obtained.

The stereochemical assignments for **10**–**13** are based on $^1$H NMR data: the stable conformers have *anti*-arranged methine hydrogens (Figure 2), as evidenced by their respective coupling constants: $J$ = 8.5 Hz for **10**, with 5 and 3% NOE at $CH_2CO_2Et$ upon irradiation of $CH_3C{=}CH_2$, and $J$ = 8 Hz for **11**, with 6% NOE for $CH_3C{=}CH_2$ on irradiation of the $CH_3CH$ group. The conformational preference in the nitropropene adducts was assigned on the basis of similar evidence ($J$ = 9.5 Hz and $J$ = 8 Hz for the methine protons in **12** and **13**, respectively) and the stereochemistry of **13**-*syn* was then deduced from the NOE data (Figure 2).

Cyclopentannulations involving nitrostyrenes **14a**–**e** were characterized by a better stereoselectivity in the ring-closure step, as compared with the aliphatic analogs, leading mainly to the trans–trans substituted methylenecyclopentanes **16** (Table IV), but the overall yields were somewhat lower, due to the reluctance of *syn*-stereomers **15** to cyclize, even at higher reaction temperature. Only negligible $\gamma$-addition of lithiated **1** to nitrostyrenes to give **17** was occasionally evidenced by the presence of a vinyl proton singlet at $\delta$ 6.2–6.4 in the $^1$H NMR spectrum of the crude products (<5%). Hence, the regiochemical outcome of conjugate additions of **1** to aromatic nitroolefins is different from that of lithiated **9**, which proceeded mainly at the unsubstituted terminus of the allylic anion.[16] The negative charge localization at the $\alpha$-position of the donor **1** in the presently described reactions may tentatively be attributed to the inductive effect of bromine. Stereochemical assignments for the cyclized products **16** are based on NOE data as shown for **16a**.




Stereoisomers **18** ($\delta$ 5.31, td, $J$ = 7, 4 Hz) were detected in minor amounts (0.2–2%). As observed for the aliphatic **3f**, the presence of a methyl substituent $\alpha$ to the nitro group resulted in stereoselective *anti* conjugate additions to give solely cyclized products **19** and **20** (5:1) in 48% yield, the stereochemistry being secured by NOE experiments (eq 2).

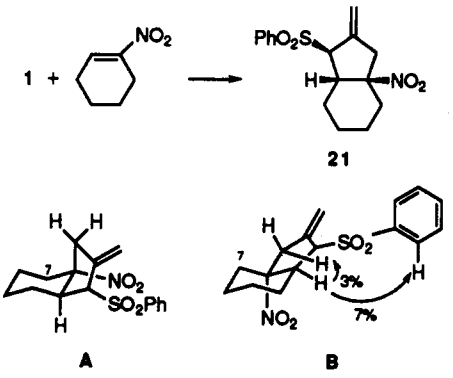



(2)

Methylenecyclopentannulation using cyclic electrophilic systems as acceptors is of synthetic interest and may lead to useful bicyclic or polycyclic intermediates. Such reactions, leading to perhydrindanes have been previously explored by transition-metal-catalyzed [3 + 2] cycloadditions and resulted in low yields unless the enones serving as acceptors were additionally activated[3,18] or more complex conjunctive reagents were used.[19] We found that bromo sulfone **1** reacts readily with the commercially available 1-nitrocyclohexene to give the stereohomogeneous hydrindane derivative **21** in 53% yield. The stereochemistry assigned for **21** is based on the preferred *cis*-junction for annulated methylenecyclopentanes[3] while the *cis*-relationship between the sulfone group and the methine proton at the ring junction is evidenced by a 7% NOE observed between the latter and the ortho-proton of the phenyl group. Of the two depicted conformations A and B, the latter is tentatively preferred because of the 3% NOE observed between the ring junction proton and one of the protons of the allylic methylene group. Moreover, a W effect was observed for one of the protons at C-7

(18) Cleary, D. G.; Paquette, L. A. *Synth. Commun.* **1987**, *17*, 497.
(19) Trost, B. M.; Mignani, S. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1988**, *110*, 1602.

(δ 2.4, $J$ = 2 Hz), due to the long-range coupling with the ring-junction proton, consistent with conformation B.




In summary, we have shown the feasibility of a tandem [3 + 2] annulation involving nitroolefins as Michael acceptors, thus providing a first example of direct intramolecular trapping of the resulting nitronates by an allylic halide group. The ease of the cyclization step depended on the stereochemical outcome of the conjugate addition and occurred with more difficulty for the *syn*-adducts to give more hindered *cis*-2-(phenylsulfonyl)-3-alkyl (or aryl) cyclopentane derivatives. Base-induced equilibration in the reaction vessel can provide stereohomogeneous methylenecyclopentanes with three stereogenic centers in one operation from readily available substrates. The studied annulation can also lead to bicyclic systems as proven by the addition of bromo sulfone 1 to 1-nitrocyclohexene to give a hydrindane derivative. An attempt to explain the differences in the stereochemical outcome of conjugate additions to nitroolefins *vs* unsaturated esters was made by using an analog of 1 devoid of bromide, namely **9** as the donor, in the absence and presence of HMPA. The results evidenced the ability of chelation with Li in the transition state with ethyl crotonate but not with 1-nitropropene, thus providing a possible explanation for the high stereoselectivity achieved in reactions with the former acceptors.

## Experimental Section

**General.**[20] Aliphatic nitroolefins were prepared via the nitroaldol reaction[21] followed by olefination according to ref 10 with some modifications to improve yields: the reactions were conducted at −40 °C (instead of 0 °C), the dilution in $CH_2Cl_2$ was increased (×2) and the amount of TEA was decreased (2 equiv). Nitroethylene,[22] nitrostyrenes,[23] and *p*-chloronitrostyrene[24] were obtained as described.

**General Procedure for the Michael Addition of Bromo Sulfone 1 to Nitroolefins 3a–e (cf. Table I).** To a stirred solution of LDA, prepared from 0.07 mL (0.5 mmol) of diisopropylamine and 0.30 mL of *n*-BuLi (0.46 mmol, 1.52 N in hexane) in 2 mL of THF was added dropwise at −100 °C a solution of 1 (100 mg, 0.36 mmol) in 0.5 mL of THF. After stirring for 10 min at the above temperature, the nitroolefin (0.4 mmol) in 0.5 mL of THF was added dropwise. After 5 min 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 brine, dried ($MgSO_4$), and evaporated under reduced pressure. Chromatographic purification of the residue (EtOAc/$CH_2Cl_2$/petroleum ether, 1:1:5) gave an inseparable mixture of **4**-*syn* and **5**-*anti* stereoisomers in yields indicated in Table I. The **4**/**5** ratio was established by integrated $^1$H NMR spectra of the initially obtained oils. Compounds **4** were isolated in pure form from reactions described further (Table II), whereas the $^1$H and $^{13}$C NMR spectra of **5** diastereomers (**5a**, **5b**, **5d**) were determined by subtracting the corresponding signals of **4** in the stereomeric mixture. Compounds **5c** and **5e** were isolated by crystallization (petroleum ether–EtOAc) from the respective stereoisomeric mixtures.

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-methyl-5-nitro-3-(phenylsulfonyl)-1-pentene 4a (*syn*):** oil; $^1$H NMR δ 7.89–7.54 (m, 5H), 5.66 (d, $J$ = 1 Hz, 1H), 5.43 (s, 1H), 5.07 (dd, $J$ = 13, 5 Hz, 1H), 4.69 (dd, $J$ = 13, 8 Hz, 1H), 3.94 (d, $J$ = 9 Hz, 1H), 3.75 (d, $J$ = 11 Hz, 1H), 3.46 (dd, $J$ = 11, 1 Hz, 1H), 3.20–3.03 (m, 1H), 1.22 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.07 (s), 136.22 (s), 134.35 (d), 129.56 (d, 2 × CH), 129.14 (d, 2 × CH), 124.72 (t), 78.89 (t), 68.90 (d), 35.93 (t), 32.16 (d), 15.94 (q); MS $m/z$ (rel inten) 364, 362 ($MH^+$, 23, 23), 282 (34), 222, 220 (100, 98), 125 (34).

**(3*RS*,4*SR*)-2-(Bromomethyl)-4-methyl-5-nitro-3-(phenylsulfonyl)-1-pentene (5a)(*anti*):** $^1$H NMR δ 7.96–7.50 (m, 5H) 5.68 (bs, 1H), 5.63 (s, 1H), 4.88 (dd, $J$ = 13, 4 Hz, 1H), 4.36 (dd, $J$ = 13, 9 Hz, 1H), 3.84 (d, $J$ = 8 Hz, 1H), 3.78 (d, $J$ = 11 Hz, 1H), 3.55 (dd, $J$ = 11, 1 Hz, 1H), 3.21–3.03 (m, 1H), 1.40 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.9 (s), 136.8 (s), 134.2 (d), 129.4 (d, 2 × CH), 129.1 (d, 2 × CH), 134.0 (t), 79.2 (t), 69.1 (d), 36.3 (t), 33.5 (t), 16.4 (q); MS $m/z$ 364, 362 ($MH^+$, 100, 82), 318, 316 (1,3), 222, 220 (4,4). Anal. **4a** + **5a** calcd for $C_{13}H_{16}BrNO_4S$: C, 43.10; H, 4.45; N, 3.86. Found: C, 43.56; H, 4.41; N, 3.67.

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-(nitromethyl)-3-(phenylsulfonyl)-1-hexene (4b)(*syn*):** oil; $^1$H NMR δ 7.91–7.52 (m, 5H), 5.65 (d, $J$ = 0.5 Hz, 1H), 5.55 (s, 1H), 4.98 (dd, $J$ = 14, 6 Hz, 1H), 4.91 (dd, $J$ = 14, 6 Hz, 1H), 4.18 (d, $J$ = 8 Hz, 1H), 3.75 (dd, $J$ = 11, 0.5 Hz, 1H), 3.51 (dd, $J$ = 11, 0.5 Hz, 1H), 2.83 (ttd, $J$ = 8, 6, 4 Hz, 1H), 1.96 (dqd, $J$ = 15, 7, 4 Hz, 1H), 1.50 (ddq, $J$ = 15, 8, 7 Hz, 1H), 1.00 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.7 (s), 136.5 (s), 134.3 (d), 129.4 (d, 2 × CH), 129.1 (d, 2 × CH), 125.0 (t), 75.1 (t), 67.9 (d), 38.9 (d), 35.3 (t), 22.3 (t), 11.2 (q); MS $m/z$ 378, 376 ($MH^+$, 36, 33), 331, 329 (10, 9), 236, 234 (91, 100).

**(3*RS*,4*SR*)-2-(Bromomethyl)-4-(nitromethyl)-3-(phenylsulfonyl)-1-hexene (5b)(*anti*):** $^1$H NMR δ 7.92–7.53 (m, 5H), 5.68 (s, 2H), 5.03 (dd, $J$ = 13.5, 5 Hz, 1H), 4.42 (dd, $J$ = 13.5, 8 Hz, 1H), 3.90 (d, $J$ = 6 Hz, 1H), 3.79 (dd, $J$ = 11, 0.5 Hz, 1H), 3.64 (dd, $J$ = 11, 0.5 Hz, 1H), 3.07–2.94 (m, 1H), 1.83 (quintet d, $J$ = 7, 2 Hz, 2H), 0.98 (t, $J$ = 7 Hz, 3H); $^{13}$C δ 137.7 (s), 136.2 (s), 134.3 (d), 129.4 (d, 2 × CH), 129.1 (d, 2 × CH), 124.3 (t), 76.6 (t), 66.1 (d), 39.1 (d), 36.6 (t), 22.6 (t), 10.5 (q); MS $m/z$ 378, 376 ($MH^+$, 9,9) 331, 329 (7, 6), 296, 234 (97, 100). Anal. **4b** + **5b** calcd for $C_{14}H_{18}BrNO_4S$: C, 44.69; H, 4.82; N, 3.72. Found: C, 45.01; H, 4.77; N, 3.63.

**(3*SR*,4*SR*)-2-(Bromomethyl)-5-methyl-4-(nitromethyl)-3-(phenylsulfonyl)-1-hexene (4c) (*syn*):** mp 104 °C; $^1$H NMR δ 7.88–7.51 (m, 5H), 5.60 (bs, 1H), 5.55 (s, 1H), 5.22 (dd, $J$ = 15, 4 Hz, 1H), 4.72 (dd, $J$ = 15, 7.5 Hz, 1H), 4.04 (d, $J$ = 8 Hz, 1H), 3.81 (dd, $J$ = 11, 0.5 Hz, 1H), 3.62 (dd, $J$ = 11, 0.5 Hz, 1H), 3.06–2.94 (m, 1H), 2.29 (d septet, $J$ = 10, 7 Hz, 1H), 1.06 (d, $J$ = 7 Hz, 3H), 0.93 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.5 (s), 137.2 (s), 134.3 (d), 129.4 (d, 2 × CH), 129.0 (d, 2 × CH), 124.4 (t), 73.6 (t), 67.8 (d), 43.3 (d), 35.0 (t), 29.1 (d), 21.5 (q); 17.7 (q); MS $m/z$ 392, 390 ($MH^+$, 88, 78), 374, 372 (9, 8), 345, 343 (10, 9), 310 (29), 250 (100).

**(3*RS*,4*SR*)-2-(Bromomethyl)-5-methyl-4-(nitromethyl)-3-(phenylsulfonyl)-1-hexene (5c) (*anti*):** mp 90 °C; $^1$H NMR δ 7.91–7.53 (m, 5H), 5.64 (s, 1H), 5.58 (s, 1H), 4.81 (dd, $J$ = 13, 4 Hz, 1H), 4.42 (dd, $J$ = 13, 6.5 Hz, 1H), 4.01 (d, $J$ = 8 Hz, 1H), 3.80 (d, $J$ = 11 Hz, 1H), 3.62 (d, $J$ = 11 Hz, 1H), 3.24–3.13 (m, 1H), 2.47 (d septet, $J$ = 10, 7 Hz, 1H), 0.99 (d, $J$ = 7 Hz, 3H), 0.93 (d, $J$ = 7Hz, 3H); $^{13}$C NMR δ 137.3 (s), 136.1 (s), 134.3 (d), 129.5 (d, 2 × CH), 129.1 (d, 2 × CH), 124.6 (t), 74.1 (t), 66.4 (d), 42.1 (d), 37.5 (t), 29.0 (d), 20.8 (q), 17.0 (q); MS $m/z$ 392, 390 ($MH^+$, 23, 19), 250, 248 (100, 93) 232, 230 (9, 8), 203, 201 (46, 45). Anal. Calcd for C15H20BrNO4S: C, 46.16; H, 5.16; N, 3.59. Found: C, 46.36; H, 5.04; N, 3.57.

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-(nitromethyl)-3-(phenylsulfonyl)-1-nonene (4d)(*syn*):** oil; $^1$H NMR δ 7.88–7.51 (m 5H),

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(21) See *Houben-Weyl, Methoden der organischen Chemie*; Georg Thieme Verlag: Stuttgart, 1971; Vol 10/1, p 246 ff.
(22) Rangathan, D.; Bhushan, Rao, C.; Rangathan, S.; Mehrotra, A. K.; Iyengar, R. *J. Org. Chem.* **1980**, *45*, 1185.
(23) Gairaud, C. B.; Lappin, G. R. *J. Org. Chem.* **1951**, *18*, 1.
(24) Campbell, N.; Anderson, W.; Gilmore, J. *J. Chem. Soc.* **1940**, 446.

5.65 (d, $J$ = 0.5 Hz, 1H), 5.55 (s, 1H), 4.97 (dd, $J$ = 12.5, 5.5 Hz, 1H), 4.87 (dd, $J$ = 12.5, 5.5 Hz, 1H), 4.19 (d, $J$ = 8 Hz, 1H), 3.76 (dd, $J$ = 11, 0.5 Hz, 1H), 3.51 (dd, $J$ = 11, 0.5 Hz, 1H), 2.95–2.81 (m, 1H), 1.96–1.81 (m, 1H), 1.56–1.17 (m, 7H), 0.87 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.6 (s), 136.4 (s), 134.4 (d), 129.4 (d, 2 × CH), 129.2 (d, 2 × CH), 126.0 (t), 75.4 (t), 67.8 (d), 37.4 (d), 35.5 (t), 31.5 (t), 29.1 (t), 26.4 (t), 22.4 (t), 13.9 (q); MS $m/z$ 420, 418 ($MH^+$, 87, 74), 338 (71), 278, 276 (100, 89).

**(3*RS*,4*SR*)-2-(Bromomethyl)-4-(nitromethyl)-3-(phenylsulfonyl)-1-nonene (5d)(*anti*)**: $^1$H NMR δ 7.93–7.50 (m, 5H), 7.69 (s, 2H), 5.09 (dd, $J$ = 13, 4.5 Hz, 1H), 4.40 (dd, $J$ = 13, 8.5 Hz, 1H), 4.00 (d, $J$ = 6 Hz, 1H), 3.81 (d, $J$ = 11 Hz, 1H), 3.70 (d, $J$ = 11 Hz, 1H), 3.11–2.97 (m, 1H), 1.81–1.61 (m, 2H), 1.50–1.12 (m, 6H), 0.87 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.8 (s), 136.4 (s), 134.3 (d), 129.4 (d, 2 × CH), 129.2 (d, 2 × CH), 124.3 (t), 77.0 (t), 66.2 (d), 37.6 (d), 36.8 (t), 31.2 (t), 29.5 (t), 26.4 (t), 22.4 (t), 13.9 (q); MS $m/z$ 420, 418 ($MH^+$, 67, 69), 338 (34), 278, 276 (100, 92).

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-(methoxymethyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (4e) (*syn*)**: oil; $^1$H NMR δ 7.87–7.51 (m, 5H), 5.67 (d, $J$ = 0.5 Hz, 1H), 5.52 (s, 1H), 5.24 (dd, $J$ = 14, 4.5 Hz, 1H), 4.95 (dd, $J$ = 14, 8 Hz, 1H), 4.10 (d, $J$ = 9.5 Hz, 1H), 3.70 (dd, $J$ = 11, 0.5 Hz, 1H), 3.56–3.44 (m, 3H), 3.27 (s, 3H), 3.20 (tq, $J$ = 9, 4.5 Hz, 1H); $^{13}$C NMR δ 137.0 (s), 136.4 (s), 134.3 (d), 129.5 (d, 2 × CH), 129.0 (d, 2 × CH), 124.4 (t), 74.0 (t), 69.6 (t), 66.3 (d), 58.8 (q), 37.9 (d), 34.8 (t); MS $m/z$ 411, 409 ($MH_2O^+$, 100, 88), 394, 392 ($MH^+$, 40, 36), 362, 360 (29, 26), 312 (17.5), 252, 250 (15, 14).

**(3*RS*,4*SR*)-2-(Bromomethyl)-4-(methoxymethyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (5e) (*anti*)**: mp 85 °C; $^1$H NMR δ 7.91–7.52 (m, 5H), 5.70 (s, 1H), 5.65 (s, 1H), 4.81 (dd, $J$ = 13, 4 Hz, 1H), 4.70 (dd, $J$ = 13, 9 Hz, 1H), 4.19 (d, $J$ = 8 Hz, 1H), 3.83 (d, $J$ = 11 Hz, 1H), 3.75 (dd, $J$ = 10, 5 Hz, 1H), 3.62 (d, $J$ = 11 Hz, 1H), 3.52 (dd, $J$ = 10, 4 Hz, 1H), 3.33 (ddt, $J$ = 8, 5, 4 Hz, 1H), 3.20 (s, 3H); $^{13}$C NMR δ 137.8 (s), 136.3 (s), 134.2 (d), 129.3 (d, 2 × CH), 129.1 (d, 2 × CH), 124.1 (t), 74.4 (t), 69.2 (t), 64.7 (d), 58.8 (q), 37.9 (d), 36.6 (t); MS $m/z$ 394, 392 ($MH^+$, 51, 46), 362, 360 (100, 88), 312 (44), 252, 250 (50, 50).

**2-(Bromomethyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (4g)**: oil; $^1$H NMR δ 7.92–7.55 (m, 5H), 5.69 (s, 1H), 5.27 (s, 1H), 4.47 (t, $J$ = 7 Hz, 2H), 4.04 (d, $J$ = 10.5 Hz, 1H), 4.01 (dd, $J$ = 11, 4 Hz, 1H), 3.92 (d, $J$ = 10.5 Hz, 1H), 2.74 (ddd, $J$ = 15, 7.5, 4 Hz, 1H), 2.40 (ddd, $J$ = 15, 11, 7 Hz, 1H); $^{13}$C NMR δ 136.4 (s), 135.8 (s), 134.5 (d), 129.3 (d, 4 × CH), 123.0 (t), 71.2 (t), 63.8 (d), 36.6 (t), 25.7 (t); MS $m/z$ 250, 248 (18, 16), 268 (13), 208, 206 (32, 28), 102 (23), 86, 84 (68, 100).

**Reactions of Bromo Sulfone 1 and Nitroolefins 3 with Ring Closure to 6a–f and 7a–f of 5-*anti* Michael Adducts. General Procedure.** The initial conditions and amounts given above were utilized. Upon completion of the nitroolefin addition, a mixture of HMPA (1 mL) and THF (0.5 mL) was added dropwise at −100°. The mixture was stirred for an additional 2 h at -78 °C and then quenched with aqueous AcOH (20%), poured into water, and extracted with $CH_2Cl_2$ as above. Column chromatography (EtOAc/$CH_2Cl_2$/petroleum ether 1:1:5) gave first the open-chain *syn*-isomers 4 and then successively cyclopentanes 7 and 6; the products 4e, 6e, and 7e were separated using petroleum ether/EtOAc (2:1) as eluents. The cyclopentanes (isolated yields given in Table II) were crystallized from petroleum ether/EtOAc.

**(2*SR*,3*RS*,4*SR*)-3-Methyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (6a)**: mp 108 °C; $^1$H NMR δ 7.97–7.55 (m, 5H), 5.35 (q, $J$ = 2 Hz, 1H), 5.18 (q, $J$ = 2 Hz, 1H), 4.36 (q, $J$ = 9.5 Hz, 1H), 3.63 (dq, $J$ = 7, 2 Hz, 1H), 3.16 (dqd, $J$ = 9.5, 7, 6.5 Hz, 1H), 2.85 (dt, $J$ = 9, 2 Hz, 2H), 1.20 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.1 (s), 136.4 (s), 134.3 (d), 129.7 (d, 2 × CH), 129.3 (d, 2 × CH), 118.2 (t), 88.6 (d), 73.2 (d), 41.0 (d), 39.2 (t), 18.6 (q); MS $m/z$ 282 ($MH^+$, 56), 235 (17), 143 (36), 125 (26), 109 (70), 93 (100). Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.75; H, 5.32; N, 4.62.

**(2*SR*,3*RS*,4*RS*)-3-Methyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (7a)**: mp 92 °C; $^1$H NMR δ 7.98–7.55 (m, 5H), 5.31 (dt, $J$ = 3, 1.5 Hz, 1H), 5.04 (td, $J$ = 6, 3 Hz, 1H), 5.04 (dt, $J$ = 2, 1 Hz, 1H), 3.91 (dq, $J$ = 7, 1.5 Hz, 1H), 3.08 (sextet, $J$ = 7 Hz, 1H), 2.93 (ddt, $J$ = 17, 3; 1.5 Hz, 1H), 2.82 (ddq, $J$ = 17, 6.5, 2 Hz, 1H), 1.05 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 139.5 (s), 137.0 (s), 134.2 (d), 129.4 (d, 2 × CH), 129.3 (d, 2 × CH), 116.9 (t), 88.8 (d), 73.0 (d), 40.1 (d), 38.4 (t), 14.6 (q); MS $m/z$ 282 ($MH^+$, 28), 264 (20), 235 (27), 143 (45), 125 (27), 109 (60), 93 (100).

**(2*SR*,3*RS*,4*SR*)-3-Ethyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (6b)**: mp 118 °C; $^1$H NMR δ 7.97–7.55 (m, 5H), 5.30 (dt, $J$ = 3, 1.5 Hz, 1H), 5.05 (dt, $J$ = 3, 1.5 Hz, 1H), 4.49 (dt, $J$ = 10, 7.5 Hz, 1H), 3.65 (dq, $J$ = 6, 1.5 Hz, 1H), 3.27 (quintet, $J$ = 6.5 Hz, 1H), 2.93 (dddt, $J$ = 15, 10, 3, 1.5 Hz, 1H), 2.85 (brdd, $J$ = 15, 7.5 Hz, 1H), 1.61 (quintet, $J$ = 7.5 Hz, 2H), 0.89 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR δ 138.0 (s), 136.9 (s), 134.3 (d), 129.8 (d, 2 × CH), 129.2 (d, 2 × CH), 118.0 (t), 87.2 (d), 72.3 (d), 46.3 (d), 39.4 (t), 26.9 (t), 10.5 (q); MS $m/z$ 296 ($MH^+$, 100), 249 (29), 171 (11), 154 (11), 123 (19), 107 (88). Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.70; H, 5.5; N, 4.55.

**(2*SR*,3*RS*,4*RS*)-3-Ethyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (7b)**: mp 107 °C; $^1$H NMR δ 7.95–7.55 (m, 5H), 5.29 (dt, $J$ = 2.5, 2 Hz, 1H), 5.19 (ddd, $J$ = 10, 6, 4 Hz, 1H), 4.98 (dt, $J$ = 2.5, 2 Hz, 1H), 3.96 (dq, $J$ = 7, 2 Hz, 1H), 2.94–2.79 (m, 1H), 1.53 (dqd, $J$ = 14, 7.5, 6.5 Hz, 1H), 1.38 (dqd, $J$ = 14, 9.5, 7.5 Hz, 1H), 0.89 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 139.4 (s), 136.9 (s), 134.1 (d), 129.4 (d, 2 × CH) 129.2 (d, 2 × CH), 117.0 (t), 87.0 (d), 71.5 (d), 47.2 (d), 38.9 (t), 22.7 (t), 12.1 (q); MS $m/z$ 296 ($MH^+$, 76), 278 (46), 249 (38), 154 (57), 107 (100).

**(2*SR*,3*RS*,4*SR*)-3-Isopropyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (6c)**: mp 120 °C; $^1$H NMR δ 7.95–7.53(m, 5H), 5.24 (td, $J$ = 3, 1.5 Hz, 1H), 4.92 (dt, $J$ = 3, 1.5 Hz, 1H), 4.63 (ddd, $J$ = 10, 8, 6.5 Hz, 1H), 3.70 (brd, $J$ = 5 Hz, 1H), 3.37 (q, $J$ = 6 Hz, 1H), 3.03 (dddd, $J$ = 15, 10, 3, 1.5 Hz, 1H), 2.89 (brdd, $J$ = 15, 8 Hz, 1H), 1.88 (octet, $J$ = 7 Hz, 1H), 0.90 (d, $J$ = 7 Hz, 3H), 0.88 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 139.1 (s), 136.3 (s), 134.2 (d), 129.8 (d, 2 × CH), 129.1 (d, 2 × CH), 117.5 (t), 85.4 (d), 71.6 (d), 50.2 (d), 39.4 (t), 31.3 (d), 19.5 (q), 18.5 (q); MS $m/z$ 310 ($MH^+$, 37), 263 (19), 171 (12), 137 (10), 121 (100).

**(2*SR*,3*RS*,4*SR*)-1-Methylene-4-nitro-3-pentyl-2-(phenylsulfonyl)cyclopentane (6d)**: mp 97 °C; $^1$H NMR δ 7.92–7.53 (m, 5H), 5.31 (dt, $J$ = 3, 1.5 Hz, 1H), 5.07 (dt, $J$ = 3, 1.5 Hz, 1H), 4.48 (dt, $J$ = 10, 8.5 Hz, 1H), 3.64 (dq, $J$ = 6.5, 1.5 Hz, 1H), 3.31 (quintet, $J$ = 7 Hz, 1H), 2.94 (dddt, $J$ = 15, 10, 3, 1.5 Hz, 1H), 2.86 (dd, $J$ = 15, 7 Hz, 1H), 1.62–1.42 (m, 2H), 1.31–1.10 (m, 6H), 0.85 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 137.9 (s), 136.3 (s), 134.2 (d), 129.7 (d, 2 × CH), 129.1 (d, 2 × CH), 118.0 (t), 87.8 (d), 72.8 (d), 45.0 (d), 39.4 (t), 34.3 (t), 31.4 (t), 25.7 (t), 22.3 (t), 13.9 (q); MS $m/z$ 338 ($MH^+$, 100), 291 (5), 149 (9). Anal. Calcd for $C_{17}H_{23}NO_4S$: C, 60.50; H, 6.87; N, 4.15. Found: C, 60.68; H, 6.64; N, 3.93.

**(2*SR*,3*RS*,4*RS*)-1-Methylene-4-nitro-3-pentyl-2-(phenylsulfonyl)cyclopentane (7d)**: mp 55 °C; $^1$H NMR δ 7.96–7.54 (m, 5H), 5.31 (q, $J$ = 2 Hz, 1H), 5.17 (td, $J$ = 6, 3.5 Hz, 1H), 5.04 (q, $J$ = 2 Hz, 1H), 3.95 (dq, $J$ = 7, 1.5 Hz, 1H), 2.96–2.81 (m, 3H), 1.48–1.04 (m, 8H), 0.84 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR δ 139.1 (s), 136.8 (s), 134.1 (d), 129.3 (d, 2 × CH), 129.2 (d, 2 × CH), 117.0 (t), 87.1 (d), 71.5 (d), 45.5 (d), 38.8 (t), 31.2 (t), 29.3 (t), 27.0 (t), 22.2 (t), 13.8 (q); MS $m/z$ 338 ($MH^+$, 100), 291 (18), 196 (5), 149 (17.5).

**(2*SR*,3*RS*,4*SR*)-3-(Methoxymethyl)-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (6e)**: mp 72–74 °C; $^1$H NMR δ 7.95 –7.54 (m, 5H), 5.31 (ddd, $J$ = 2.5, 1.5, 1 Hz, 1H), 5.08 (ddd, $J$ = 3, 1.5, 1 Hz, 1H), 4.80 (dt, $J$ = 11, 8 Hz, 1H), 4.02 (dq, $J$ = 6.5, 1.5 Hz, 1H), 3.55 (dd, $J$ = 10, 3 Hz, 1H), 3.44–3.33 (m, 2H), 3.31 (s, 3H), 2.86 (brdd, $J$ = 14.5, 7.5 Hz, 1H), 2.78 (ddq, $J$ = 14, 11, 2.5 Hz, 1H); $^{13}$C NMR δ 137.4 (s), 136.3 (s), 134.3 (d), 129.8 (d, 2 × CH), 129.2 (d, 2 × CH), 117.8 (t), 83.2 (d), 70.7 (t), 68.5 (d), 59.2 (q), 45.9 (d), 39.2 (t); MS $m/z$ 312 ($MH^+$, 100), 265 (80), 233 (63), 121 (23), 123 (66). Anal. Calcd for $C_{14}H_{17}NO_5S$: C, 54.00; H, 5.50; N, 4.50. Found: C, 54.30; H, 5.31; N, 4.50.

**(2*SR*,3*RS*,4*RS*)-3-(Methoxymethyl)-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (7e)**: mp 106 °C; $^1$H NMR δ 7.95–7.53 (m, 5H), 5.31 (dt, $J$ = 2.5, 1.5 Hz, 1H), 5.15 (td, $J$ = 6.5, 3 Hz, 1H), 5.03 (quintet, $J$ = 1.5 Hz, 1H), 4.08 (dq, $J$ = 7, 1.5 Hz, 1H), 3.51 (dd, $J$ = 9, 5.5 Hz, 1H), 3.32 (dd, $J$ = 9, 6 Hz, 1H), 3.23 (dq, $J$ = 7, 6.5 Hz, 1H), 3.20 (s, 3H), 2.88 (dddt, $J$ = 17, 3, 2.5, 1.5 Hz, 1H), 2.77 (ddq, $J$ = 17, 6.5, 2.5 Hz, 1H); $^{13}$C NMR δ 139.1 (s), 136.5 (s), 134.2 (s), 129.5 (d, 2 × CH), 129.2 (d, 2 × CH), 117.2 (t), 85.7 (d), 70.2 (t), 68.9 (d), 59.0 (q), 45.1 (d), 39.1 (t); MS $m/z$ 312 ($MH^+$, 43), 280 (100), 279 (53).

**(2*SR*,3*RS*,4α-*SR*,4β-*RS*)-3-Methyl-4β-methyl-1-methylene-4α-nitro-2-(phenylsulfonyl)cyclopentane (6f):** mp 96 °C; $^1$H NMR δ 7.95–7.55 (m, 5H), 5.33 (tt, *J* = 2, 1 Hz, 1H), 5.19 (tt, *J* = 2, 1 Hz, 1H), 3.59 (dq, *J* = 8, 1 Hz, 1H), 3.28 (quintet, *J* = 7 Hz, 1H), 2.94 (brd, *J* = 14 Hz, 1H), 2.53 (d, *J* = 14 Hz, 1H), 1.46 (s, 3H), 1.12 (d, *J* = 7 Hz, 3H); $^{13}$C NMR δ 137.7 (s), 136.3 (s), 134.2 (d), 129.7 (d, 2 × CH), 129.1 (d, 2 × CH), 117.7 (t), 91.1 (s), 72.8 (d), 46.7 (t), 43.3 (d), 19.3 (q), 14.4 (q); MS *m/z* 296 ($MH^+$, 1), 249 (100), 230 (9), 183 (26). Anal. Calcd for $C_{14}H_{17}NO_4S$: C, 56.93; H, 5.80; N, 4.74. Found: C, 57.01; H, 5.66; N, 4.75.

**(2*SR*,3*RS*,4α-*RS*,4β-*SR*)-3-Methyl-4α-methyl-1-methylene-4β-nitro-2-(phenylsulfonyl)cyclopentane (7f):** mp 139 °C; $^1$H NMR δ 7.96–7.55 (m, 5H), 5.22 (ddd, *J* = 3, 2, 1 Hz, 1H), 4.96 (ddd, *J* = 3, 2, 1 Hz, 1H), 4.03 (dq, *J* = 8.5, 2 Hz, 1H), 2.84 (dt, *J* = 17, 1 Hz, 1H), 2.75 (dd, *J* = 8.5, 7 Hz, 1 H), 2.67 (dq, *J* = 17, 2.5 Hz, 1H), 2.21 (s, 3H), 1.55 (d, *J* = 7 Hz, 3H); $^{13}$C NMR δ 140.1 (s) 137.3 (s), 134.1 (d), 129.5 (d, 2 × CH), 129.2 (d, 2 × CH), 115.4 (t), 95.4 (s), 73.8 (d), 47.5 (t), 46.4 (d), 21.9 (q), 13.6 (q); MS *m/z* 313 ($MH_2O^+$, 100), 249 (66), 124 (7), 107 (21).

**(3*SR*,4*SR*,5*SR*)-2-(Bromomethyl)-4-methyl-5-nitro-3-(phenylsulfonyl)-1-hexene (4f) (*syn*):** mp 87 °C; $^1$H NMR δ 7.90–7.53 (m, 5H), 5.66 (s, 1H), 5.58 (dq, *J* = 7, 3 Hz, 1H), 5.52 (s, 1H), 4.39 (d, *J* = 9 Hz, 1H), 3.63 (d, *J* = 11.5 Hz, 1H), 3.41 (d, *J* = 11.5 Hz, 1H), 2.86–2.73 (m, 1H), 1.63 (d, *J* = 7 Hz, 3H), 1.09 (d, *J* = 7 Hz, 3H); $^{13}$C NMR δ 137.7 (s), 136.3 (s), 134.2 (d), 129.5 (d, 2 × CH), 129.1 (d, 2 × CH), 125.2 (t), 83.4 (d), 68.5 (d), 37.1 (d), 35.5 (t), 17.5 (q), 11.9 (q); MS *m/z* 378, 376 ($MH^+$, 36, 34), 360, 358 (13, 13), 331, 329 (100, 87), 296 (52), 236, 234 (67, 66), 189, 187 (77, 82).

**NOE Experiments.** In **4f** a gauche conformation for $C_4$–$C_5$ ($J_{H_4H_5}$ = 3 Hz) gives 9% NOE for the C-4 proton when the methyl at C-5 was irradiated. In **6f** a 7% NOE was found for the C-3 methyl (δ 1.12) on irradiation of the C-4 methyl (δ 1.46) and 8% NOE for the C-2 proton when the C-3 methyl was irradiated. In **7f** a 9% NOE was determined for the C-3 proton when the C-4 methyl (δ 2.21) was irradiated.

**(2*SR*,4*SR*)-1-Methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (6g):** mp 94–96 °C; $^1$H NMR δ 8.00–7.50 (m, 5H), 5.88 (dt, *J* = 2.5, 1.5 Hz, 1H), 5.22 (dt, *J* = 3, 1.5 Hz, 1H), 4.81 (ddt, *J* = 17.5, 9.5, 8.5 Hz, 1H), 4.07 (ddq, *J* = 9, 7, 1.5 Hz, 1H), 3.15–2.86 (m, 3H), 2.82–2.61 (m, 1H); $^{13}$C NMR δ 138.0 (s), 136.7 (s), 134.2 (d), 129.5 (d, 2 × CH), 129.2 (d, 2 × CH), 117.9 (t), 81.6 (d), 66.5 (d), 38.6 (t), 31.8 (t); MS *m/z* 268 (($MH^+$, 32), 285 (100), 221 (32), 143 (16), 79 (21).

**(2*SR*,4*RS*)-1-Methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (7g):** mp 114–116 °C; $^1$H NMR δ 7.95–7.53 (m, 5H), 5.31 (dt, *J* = 3, 1.5 Hz, 1H), 5.12 (dddd, *J* = 10, 7.5, 4.5, 3.5 Hz, 1H), 5.00 (dt, *J* = 3, 1.5 Hz, 1H), 4.25 (ddq, *J* = 8, 6.5, 1.5 Hz, 1H), 3.06 (dddd, *J* = 17, 10, 3, 2 Hz, 1H), 2.94 (ddt, *J* = 17, 4.5, 1.5 Hz, 1H), 2.83–2.71 (m, 2H); $^{13}$C NMR 138.5 (s), 136.7 (s), 134.2 (d), 129.2 (d, 2 × CH), 129.2 (d, 2 × CH), 117.8 (t), 84.0 (d), 67.1 (d), 39.4 (t), 32.3 (t); MS *m/z* 268 ($MH^+$, 23), 285 (100), 221 (79), 143 (30), 79 (32). Anal. Calcd for $C_{12}H_{13}NO_4S$: C; 53.92; H, 4.90; N, 5.24. Found: C, 53.69; H, 4.69; N, 5.05.

**Reactions of Bromo Sulfone 1 and Nitroolefins 3 with Ring Closure of 5-*anti* and Partial Ring Closure of 4-*syn* Michael Adducts (cf. Table III). General Procedure.** The reactions were initially performed as shown for **6a–f** and **7a–f**. After stirring the mixture for 1 h at −78 °C, the reaction was continued for 1.5 h at −40 °C. Workup as shown before and chromatography (EtOAc/$CH_2Cl_2$/petroleum ether 1:1:5) gave first a mixture of **4** and **8** and then successively **7** and **6**. The mixture of **4** and **8** was separated by repeated chromatography ($CHCl_3$/ether/petroleum ether, 1:2:6). Isolated yields are given in Table III.

**(2*SR*,3*SR*,4*RS*)-3-Methyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (8a):** mp 77 °C; 1H NMR δ 7.88–7.50 (m, 5H), 5.28 (td, *J* = 10, 6.5 Hz, 1H), 5.03 (td, *J* = 2.5, 1 Hz, 1H), 4.35 (td, *J* = 2.5, 1 Hz, 1H), 4.05 (brd, *J* = 7 Hz, 1H), 3.33 (ddtd, *J* = 17, 10, 3, 1 Hz, 1H), 3.17 (dqd, *J* = 10, 7, 6.5 Hz, 1H), 2.91 (ddt, *J* = 17, 6.5, 1 Hz, 1H), 1.60 (d, *J* = 7 Hz, 3H); $^{13}$C NMR δ 139.1 (s), 137.5 (s), 134.0 (d), 129.1 (d, 2 × CH), 128.8 (d, 2 × CH), 117.7 (t), 89.5 (d), 72.7 (d), 44.2 (t), 36.4 (d), 13.7 (q); MS *m/z* 282 ($MH^+$, 46), 235 (100), 93 (5).

**(2*SR*,3*SR*,4*RS*)-3-Ethyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (8b):** mp 76 °C; $^1$H NMR δ 7.87–7.50 (m, 5H), 5.36 (td, *J* = 10, 6 Hz, 1H), 4.98 (td, *J* = 2.5, 1 Hz, 1H), 4.31 (ddd, *J* = 3, 2, 1 Hz, 1H), 4.12 (brd, *J* = 7 Hz, 1H), 3.37 (ddtd, *J* = 17.5, 10, 3, 1 Hz, 1H), 3.04 (ddt, *J* = 10, 7.5, 6 Hz, 1H), 2.82 (ddt, *J* = 17.5, 6, 2.5 Hz, 1H), 2.32 (ddq, *J* = 14, 9, 7 Hz, 1H), 1.87 (ddq, *J* = 14, 8, 7 Hz, 1H), 1.10 (t, *J* = 7 Hz, 3H); $^{13}$C NMR δ 139.4 (s), 137.4 (s), 134.0 (d), 128.8 (d, 2 × CH), 128.4 (d, 2 × CH), 117.5 (t), 88.6 (d), 71.8 (d), 51.9 (d), 36.7 (t), 21.8 (t), 12.6 (q); MS *m/z* 296 ($MH^+$, 48), 249 (100), 107 (68).

**(2*SR*,3*SR*,4*RS*)-3-Isopropyl-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (8c):** mp 174 °C; $^1$H NMR δ 7.86–7.48 (m, 5H), 5.48 (td, *J* = 10, 5 Hz, 1H), 4.88 (brt, *J* = 2.5 Hz, 1H), 4.30 (brt, *J* = 2.5 Hz, 1H), 4.19 (brd, *J* = 6.5 Hz, 1H), 3.51 (ddtd, *J* = 17, 10, 2.5, 1 Hz, 1H), 3.05 (td, *J* = 10, 6.5 Hz, 1H), 2.72 (d septet, *J* = 10, 6.5 Hz, 1H), 2.60 (brdd, *J* = 17, 5 Hz, 1H), 1.24 (d, *J* = 7 Hz, 3H), 0.96 (d, 7 Hz, 3H); $^{13}$C NMR δ 139.8 (s), 137.4 (s), 133.9 (d), 128.9 (d, 2 × CH), 128.7 (d, 2 × CH), 117.2 (t), 87.6 (d), 72.9 (d), 56.7 (d), 38.4 (t), 28.6 (d), 23.3 (q), 20.0 (q); MS *m/z* 310 ($MH^+$, 6), 263 (21), 121 (100).

**(2*SR*,3*SR*,4*RS*)-1-Methylene-4-nitro-3-pentyl-2-(phenylsulfonyl)cyclopentane (8d):** mp 67 °C; $^1$H NMR δ 7.86–7.47 (m, 5H), 7.70–7.61 (m, 1H), 7.59–7.47 (m, 2H), 5.36 (td, *J* = 10, 6 Hz, 1H), 4.99 (td, *J* = 2.5, 1 Hz, 1H), 4.33 (td, *J* = 2.5, 1 Hz, 1H), 4.11 (br, *J* = 7 Hz, 1H), 3.36 (ddtd, *J* = 18, 10, 2, 1 Hz, 1H), 3.09 (ddt, *J* = 10, 7, 6 Hz, 1H), 2.82 (ddt, *J* = 18, 6, 2 Hz, 1H), 2.36–2.17 (m, 1H), 1.84–1.68 (m, 1H), 1.65–1.45 (m, 1H), 1.44–1.20 (m, 5H), 0.90 (t, *J* = 7 Hz, 3H); $^{13}$C NMR δ 139.5 (s), 137.7 (s), 133.9 (d), 129.1 (d, 2 × CH), 128.8 (d, 2 × CH), 117.5 (t), 88.8 (d), 72.0 (d), 50.2 (d), 36.7 (t), 31.7 (t), 28.4 (t), 27.8 (t), 22.4 (t), 14.0 (q); MS *m/z* 338 ($MH^+$, 26), 291 (37), 149 (100), 99 (23).

**Reactions of 1 with (*E*)-1-Aryl-2-nitroethenes (14a–f).** The procedure was identical with that used for aliphatic nitroolefins (cf. Table II) starting the reaction at −100 °C and continuing at −78 °C (reaction time indicated in Table IV). The dissolution of nitroolefins **14c** and **14f** (0.4 mmol) required 3 mL of THF. The products were separated by chromatography (elution with $CH_2Cl_2$/EtOAc/petroleum ether 1:1:5) to afford first **15-*syn*** and then **16**. For the separation of **15c** from **16c** and of **15f** from **16f** petroleum ether/EtOAc 2:1 was used as eluent. Isolated yields are given in Table IV. The products were crystallized from petroleum ether/EtOAc.

**(3*SR*,4*SR*)-2-(Bromomethyl)-5-nitro-4-phenyl-3-(phenylsulfonyl)-1-pentene (15a) (*syn*):** mp 114 °C; $^1$H NMR δ 7.90–7.15 (m, 10H), 5.66 (dd, *J* = 13, 4.5 Hz, 1H), 4.49 (s, 1H), 5.44 (d, *J* = 1 Hz, 1H), 5.025 (dd, *J* = 13, 10.5 Hz, 1H), 4.25 (td, *J* = 11, 4.5 Hz, 1H), 4.12 (d, *J* = 11 Hz, 1H), 3.28 (dd, *J* = 11.5, 1 Hz, 1H), 3.03 (dd, *J* = 11.5, 1 Hz, 1H); $^{13}$C NMR δ 136.7 (s), 136.4 (s), 135.2 (s), 134.6 (d), 130.1 (d, 2 × CH), 129.1 (d, 2 × CH), 129.0 (d, 2 × CH), 128.9 (d, 2 × CH) 128.6 (d), 124.8 (t), 78.8 (t), 69.4 (d), 44.9 (d), 35.2 (t); MS *m/z* 426, 424 ($MH^+$, 24, 21), 379, 377 (18, 15), 344 (10), 284, 282 (100, 89), 237, 235 (46, 41). Anal. Calcd for $C_{18}H_{18}BrNO_4S$: C, 50.95; H, 4.28; N, 3.3. Found: C, 51.15; H, 4.19; N, 3.18.

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-(4-methoxyphenyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (15b) (*syn*):** mp 158 °C; $^1$H NMR δ 7.93–7.49 (m, 5H), 7.09 (d, *J* = 9 Hz, 2 H), 6.78 (d, *J* = 9 Hz, 2H), 5.62 (dd, *J* = 13, 4.5 Hz, 1H), 5.48 (s, 1H), 5.44 (s, 1H), 4.98 (dd, *J* = 13, 10.5 Hz, 1H), 4.22 (td, *J* = 10.5, 4.5 Hz, 1H), 4.09 (d, *J* = 10.5 Hz, 1H), 3.75 (s, 3H), 3.31 (d, *J* = 12 Hz, 1H), 3.05 (d, *J* = 12 Hz, 1H); $^{13}$C NMR δ 159.5 (s), 136.7 (s), 136.4 (s), 134.5 (d), 130.0 (d, 4 × CH), 129.0 (d, 2 × CH), 126.9 (s), 124.7 (t), 114.3 (d, 2 × CH), 78.9 (t), 69.5 (d), 55.2 (q), 44.2 (d), 35.3 (t); MS *m/z* 456, 454 ($MH^+$, 12, 11), 409, 407 (44, 39), 314, 312 (89, 100), 284, 282 (23, 26), 267 (72). Anal. Calcd for $C_{19}H_{20}BrNO_5S$: C, 50.23; H, 4.43; N, 3.08. Found: C, 50.54; H, 4.35; N, 2.91.

**(3*SR*,4*SR*)-5-(Bromomethyl)-4-(3,4-dimethoxyphenyl)-5-nitro-3-(phenylsulfonyl)-1-pentane (15c) (*syn*):** mp 81–83 °C; $^1$H NMR δ 7.92–7.52 (m, 5H), 6.86–6.67 (m, 3H), 5.63 (dd, *J* = 13, 4 Hz, 1H), 5.47 (s, 1H), 5.44 (s, 1H), 5.01 (dd, *J* = 13, 10 Hz, 1 H), 4.20 (td, *J* = 11, 4 Hz, 1H), 4.15 (d, *J* = 11 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.34 (d, *J* = 11.5 Hz, 1H), 3.12 (d, *J* = 11.5 Hz, 1H); $^{13}$C NMR δ 149.1 (2 × C), 136.6 (s), 136.5 (s), 134.6 (d), 130.0 (d, 2 × CH), 129.0 (d, 2 × CH), 127.3 (s), 124.6 (t), 121.5 (d), 112.0 (d), 111.2 (d), 78.9 (t), 69.2 (t), 56.1 (dd), 55.8 (dd), 44.6 (d), 35.6 (t); MS *m/z* 486, 484 ($MH^+$, 100, 91), 439, 437 (74, 64), 404 (7), 344, 342 (10, 7), 217, 215 (8, 83). Anal. Calcd for

$C_{20}H_{22}BrNO_6S$: C, 49.59; H, 4.58; N, 2.90. Found: C, 49.50; H, 4.72; N, 2.85.

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-(4-chlorophenyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (15d) (*syn*):** mp 158 °C; $^1$H NMR δ 7.90–7.08 (m, 9H), 5.63 (dd, *J* = 13.5, 4.5 Hz, 1H), 5.46 (d, *J* = 1 Hz, 1H), 5.41 (s, 1H), 4.97 (dd, *J* = 13.5, 11 Hz, 1H), 4.25 (td, *J* = 11, 4.5 Hz, 1H), 4.10 (d, *J* = 11 Hz, 1H), 3.28 (dd, *J* = 11, 1 Hz, 1H), 3.15 (dd, *J* = 11, 1 Hz, 1H); $^{13}$C NMR δ 136.4 (s), 136.0 (s), 134.7 (d), 134.6 (s), 133.7 (s), 130.3 (2 × CH), 130.0 (2 × CH), 129.1 (d, 2 × CH), 129.1 (d, 2 × CH), 125.1 (t), 78.5 (t), 69.1 (d), 44.1 (d), 35.2 (t); MS *m/z* 462, 460, 458 ($MH^+$, 17, 42, 28), 411 (15), 320, 318, 316 (32, 100, 68). Anal. Calcd for $C_{18}H_{17}BrClNO_4S$: C, 47.12; H, 3.74; N, 3.05. Found: C, 47.42; H, 3.93; N, 2.91.

**(3*SR*,4*SR*)-5-(Bromomethyl)-4-(4-methylphenyl)-5-nitro-3-(phenylsulfonyl)-1-pentene (15e) (*syn*):** mp 160 °C; $^1$H NMR δ 7.92–7.06 (m, 9H), 5.63 (dd, *J* = 13, 4.5 Hz, 1H), 5.47 (s, 1H), 5.43 (d, *J* = 1 Hz, 1H), 4.99 (dd, *J* = 13, 10.5 Hz, 1H), 4.21 (td, *J* = 10.5, 4.5 Hz, 1H), 4.11 (d, *J* = 11 Hz, 1H), 3.33 (dd, *J* = 11, 1 Hz, 1H), 3.04 (dd, *J* = 11, 1 Hz, 1H), 2.28 (s, 3H); $^{13}$C NMR δ 136.4 (s), 136.8 (s), 136.5 (s), 134.5 (d), 132.1 (s), 130.1 (d, 2 × CH), 129.6 (d, 2 × CH), 129.1 (d, 2 × CH), 128.8 (d, 2 × CH), 124.8 (t), 78.9 (t), 69.4 (d), 44.6 (d), 35.3 (t), 21.1 (q); MS *m/z* 440, 438 (($MH^+$, 33, 28), 393, 391 (38, 32), 358 (12), 298, 296 (100, 14), 251, 249 (34, 34), 169 (39). Anal. Calcd for $C_{19}H_{20}BrNO_4S$: C, 52.06; H, 4.60; N, 3.19. Found: C, 52.23; H, 4.35; N, 2.91

**(3*SR*,4*SR*)-2-(Bromomethyl)-4-[3,4-(methylenedioxy)-phenyl]-5-nitro-3-(phenylsulfonyl)-1-pentene (15f) (*syn*):** mp 153 °C; $^1$H NMR δ 7.91–7.51 (m, 5H), 6.73–6.60 (m, 3H), 5.94 (s, 2H), 5.62 (dd, *J* = 13, 4.5 Hz, 1H), 5.48 (d, *J* = 1 Hz, 1H), 5.46 (s, 1H), 4.94 (dd, *J* = 13, 11 Hz, 1H), 4.17 (td, *J* = 11, 4.5 Hz, 1H), 4.06 (d, *J* = 11 Hz, 1H), 3.34 (d, *J* = 11 Hz, 1H), 3.16 (dd, *J* = 11, 1 Hz, 1H); $^{13}$C NMR δ 148.0 (s), 147.7 (s), 136.6 (s), 136.3 (s), 134.5 (d), 130.0 (d, 2 × CH), 129.0 (d, 2 × CH), 128.6 (s), 124.9 (t), 122.6 (d), 109.2 (d), 108.5 (d), 101.4 (t), 78.9 (t), 69.5 (d), 44.6 (d), 35.3 (t); MS *m/z* 470, 468 (11, 12), 423, 421 (31, 27), 388 (8), 328, 326 (100, 95). Anal. Calcd for $C_{19}H_{18}BrNO_6S$: C, 48.73; H, 3.87; N, 2.99. Found: C, 48.95; H, 3.94; N, 3.06.

**(2*SR*,3*RS*,4*SR*)-1-Methylene-4-nitro-3-phenyl-2-(phenylsulfonyl)cyclopentane (16a):** mp 102 °C; $^1$H NMR δ 7.87–6.93 (m, 10H), 5.46 (ddd, *J* = 3, 1.5, 1 Hz, 1H), 5.25 (ddd, *J* = 3, 1.5, 1 Hz, 1H), 4.86 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 4.29 (dd, *J* = 9, 7 Hz, 1H), 4.14 (dq, *J* = 7, 1.5 Hz, 1H), 3.18 (ddtd, *J* = 15, 11, 3, 1.5 Hz, 1H), 3.10 (ddt, *J* = 15, 7.5, 1 Hz, 1H); $^{13}$C NMR δ 138.6 (s), 137.3 (s), 136.6 (s), 134.1 (d), 129.4 (d, 2 × CH), 129.1 (d, 4 × CH), 128.1 (d), 127.2 (d, 2 × CH), 118.4 (t), 89.7 (d), 74.0 (d), 50.8 (d), 39.8 (t); MS *m/z* 344 (($MH^+$, 18), 297 (69), 202 (12), 171 (40), 156 (31), 155 (100). Anal. Calcd for $C_{18}H_{17}NO_4S$: C, 62.95; H, 4.99; N, 4.08. Found: C, 63.26; H, 4.98; N, 3.94.

**(2*SR*,3*RS*,4*SR*)-3-(4-Methoxyphenyl)-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (16b):** mp 118 °C; $^1$H NMR δ 7.88–6.71 (m, 9H), 5.46 (ddd, *J* = 2.5, 1.5, 1 Hz, 1H), 5.23 (ddd, *J* = 2.5, 1.5, 1 Hz, 1H), 4.81 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 4.24 (dd, *J* = 9, 7 Hz, 1H), 4.09 (dq, *J* = 7, 1.5 Hz, 1H), 3.74 (s, 3H), 3.15 (dddt, *J* = 15, 11, 2.5, 1.5 Hz, 1H), 3.05 (ddt, *J* = 15, 7.5, 1 Hz, 1H); $^{13}$C NMR δ 159.3 (s), 137.3 (s), 136.7 (s), 134.0 (d), 130.4 (s), 129.3 (d, 2 × CH), 129.1 (d, 2 × CH), 128.2 (d, 2 × CH), 118.2 (t), 114.5 (d, 2 × CH), 89.8 (d), 74.0 (d), 55.3 (q), 50.2 (d), 39.8 (t); MS *m/z* 374 ($MH^+$), 327 (100), 185 (45). Anal. Calcd for $C_{19}H_{19}NO_5S$: C, 61.10; H, 5.13; N, 3.75. Found: C, 60.81; H, 4.97; N, 3.50.

**(2*SR*,3*RS*,4*SR*)-3-(3,4-Dimethoxyphenyl)-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (16c):** mp 144 °C; $^1$H NMR δ 7.88–7.42 (m, 5H), 6.71 (d, *J* = 8 Hz, 1H), 6.55 (dd, *J* = 8, 2 Hz, 1H), 6.44 (d, *J* = 2 Hz, 1H), 5.45 (ddd, *J* = 2.5, 1.5, 1 Hz, 1H), 5.23 (ddd, *J* = 2.5, 1.5, 1 Hz, 1H), 4.85 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 4.24 (dd, *J* = 9, 6.5 Hz, 1H), 4.11 (dq, *J* = 6.5, 1.5 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.18 (dddt, *J* = 15, 11, 2.5, 1.5 Hz, 1H), 3.08 (br dd, *J* = 15, 7.5 Hz, 1H); $^{13}$C NMR δ 149.1 (s), 148.7 (s), 137.1 (s), 136.5 (s), 134.0 (d), 130.9 (s), 129.2 (d, 2 × CH), 129.0 (d, 2 × CH), 119.0 (d), 118.3 (t), 111.6 (d), 110.6 (d), 89.7 (d), 73.9 (d), 55.9 (q, 2 × $CH_3$), 50.4 (d), 39.7 (t); MS *m/z* 403 ($MH^+$, 15), 358 (23), 357 (100), 216 (29), 215 (26). Anal. Calcd for $C_{20}H_{21}NO_6S$: C, 59.54; H, 5.25; N, 3.47. Found: C, 59.41; H, 5.40; N, 3.26.

**(2*SR*,3*RS*,4*SR*)-3-(4-Chlorophenyl)-1-methylene-4-nitro-2-(phenylsulfonyl)cyclopentane (16d):** mp 124 °C; $^1$H NMR δ 7.86–6.90 (m, 9H), 5.47 (dt, *J* = 3, 1.5 Hz, 1H), 5.23 (dt, *J* = 3, 1.5 Hz, 1H), 4.80 (ddd, *J* = 11, 9, 7.5 Hz, 1 Hz), 4.28 (dd, *J* = 11, 7 Hz, 1H), 4.07 (dq, *J* = 7, 1.5 Hz, 1H), 3.17 (dddd, *J* = 15, 9, 3, 1.5 Hz, 1H), 3.09 (brdd, *J* = 15, 7.5 Hz, 1H); $^{13}$C NMR δ 136.8 (s), 136.4 (s), 134.3 (d), 134.1 (s), 129.3 (d, 4 × CH), 129.2 (d, 2 × CH), 129.0 (s), 128.6 (d, 2 × CH), 118.6 (t), 89.3 (d), 73.8 (d), 50.1 (d), 39.7 (t); MS *m/z* 378.5 ($MH^+$, 21), 331 (46), 205 (16), 191 (39), 190 (21), 189 (100). Anal. Calcd for $C_{18}H_{16}ClNO_4S$: C, 57.21; H, 4.27; N, 3.71. Found: C, 57.52; H, 4.42; N, 3.42.

**(2*SR*,3*RS*,4*SR*)-1-Methylene-3-(4-Methylphenyl)-4-nitro-2-(phenylsulfonyl)cyclopentane (16e):** mp 92 °C; $^1$H NMR δ 7.86–7.43 (m, 5H), 7.02 (d, *J* = 8 Hz, 2H), 6.86 (d, *J* = 8 Hz, 2H), 5.45 (ddd, *J* = 3, 1.4, 1 Hz, 1H), 5.23 (ddd, *J* = 3, 1.5, 1 Hz, 1H), 4.83 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 4.26 (dd, *J* = 9, 6.5 Hz, 1H), 4.10 (dq, *J* = 7, 1.5 Hz, 1H), 3.16 (dddd, *J* = 15, 9, 3,2 Hz, 1H), 3.07 (brdd, *J* = 15, 7.5 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR δ 137.8 (s), 137.4 (s), 136.6 (s), 135.5 (s), 134.0 (d), 129.7 (d, 2 × CH), 129.4 (d, 2 × CH), 129.1 (d, 2 × CH), 127.0 (d, 2 × CH), 118.2 (t), 89.7 (d), 74.1 (d), 50.4 (d), 39.8 (t), 21.0 (q); MS *m/z* 358 ($MH^+$, 7), 311 (75), 216 (10), 169 (100). Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.84; H, 5.36; N, 3.92. Found: C, 63.79; H, 5.40; N, 3.92.

**(2*SR*,3*RS*,4*SR*)-1-Methylene-3-[3,4-(methylenedioxy)-phenyl]-4-nitro-2-(phenylsulfonyl)cyclopentane (16f):** mp 169–171 °C; $^1$H NMR δ 7.88–7.54 (m, 5H), 6.62 (d, *J* = 8 Hz, 1H), 6.50–6.39 (m, 2H), 5.93 (s, 2H), 5.45 (ddd, *J* = 3, 1.5 Hz, 1H), 5.24 (ddd, *J* = 3, 1.5, 1, Hz, 1H), 4.79 (ddd, *J* = 11, 9, 7.5 Hz, 1H), 4.20 (dd, *J* = 9, 7 Hz, 1H), 4.07 (dq, *J* = 7, 2 Hz, 1H), 3.14 (dddd, *J* = 15, 9, 2.5, 1 Hz, 1H), 3.05 (brdd, *J* = 15, 7 Hz, 1H); $^{13}$C NMR δ 148.2 (s), 147.4 (s), 137.1 (s), 136.6 (s), 134.2 (d), 132.1 (s), 129.4 (d, 2 × CH), 129.2 (d, 2 × CH), 120.9 (d), 118.4 (t), 108.7 (d), 107.2 (d), 101.3 (t), 89.8 (d), 73.9 (d), 50.7 (d), 39.7 (t); MS *m/z* 388 ($MH^+$, 8), 342 (17), 341 (100), 200 (35), 199 (49). Anal. Calcd for $C_{19}H_{17}NO_6S$: C, 58.90; H, 4.42; N, 3.61. Found: C, 58.91; H, 4.13; N, 3.49.

**Reaction of 1 with (*E*)-1-Phenyl-2-methyl-2-nitroethene.** The procedure as above afforded a residue which was chromatographed (elution as above) to separate the stereomeric mixture of **19** and **20** from a polar polymeric fraction. The **19**/**20** ratio was determined by the integration of the $^1$H NMR spectrum. Compound **19** was crystallized (petroleum ether/EtOAc) from the mixture: mp 143 °C; $^1$H NMR δ 7.78–6.81 (m, 10H), 5.57 (ddd, *J* = 3,2, 1 Hz, 1H), 5.53 (tt, *J* = 2, 1 Hz, 1H), 4.53 (d, *J* = 9 Hz, 1H), 4.38 (dq, *J* = 9, 2 Hz, 1H), 3.46 (dddd, *J* = 15, 3, 2, 1 Hz, 1H), 2.75 (d, *J* = 15 Hz, 1H), 1.29 (s, 3H); $^{13}$C NMR δ 137.2 (s), 136.7 (s), 134.3 (s), 133.8 (d), 129.1 (d, 2 × CH), 128.9 (d, 2 × CH), 128.4 (d, 2 × CH), 128.3 (d, 2 × CH), 127.9 (d), 118.4 (t), 92.9 (s), 70.7 (d), 54.6 (d), 47.6 (t), 20.4 (q); MS *m/z* 311 ($MH^+ - NO_2$, 76), 191 (40), 169 (100), 81 (22). Anal. Calcd for $C_{19}H_{19}NO_4S$: C, 63.84; H, 5.36; N, 3.92. Found: C, 63.59; H, 5.10; N, 3.82.

The $^1$H NMR of stereomer **20** was obtained by subtracting the corresponding signals of **19**: δ 7.78–6.81 (m, 10H), 5.64 (dt, *J* = 3, 2 Hz, 1H), 5.48, (dt, *J* = 2, 1.5 Hz, 1H), 4.80 (dq, *J* = 10, 2 Hz, 1H), 3.74 (d, *J* = 9.5 Hz, 1H), 3.13 (brd, *J* = 17 Hz, 1H), 2.98 (dq, *J* = 17, 3 Hz, 1H), 1.66 (s, 3H); MS (**19** + **20**) *m/z* 375 (($MH_2O^+$, 48), 358 ($MH^+$, 1), 312 (17), 311 (100), 186 (22), 169 (67).

**Reactions of Methallyl Sulfone 9 with Ethyl Crotonate.** To a stirred solution of LDA, prepared from 0.07 mL (0.5 mmol) of diisopropyl amine and 0.3 mL of *n*-BuLi (0.46 mmol, 1.52 M in hexane) in 2 mL of THF was added dropwise at −100 °C a solution of **9** (71 mg, 0.36 mmol) in 0.5 mL of THF. After 10 min, ethyl crotonate was added (47 mg, 0.4 mmol) in 0.5 mL of THF and stirring was continued for 1.5 h at the above temperature to complete the conversion (TLC). Quenching (20% aqueous AcOH) and extraction ($CH_2Cl_2$) followed by evaporation under reduced pressure gave a residue, and the integration of its $^1$H NMR spectrum showed the ratio 89:11 of **10**/**11**. Chromatographic purification (EtOAc/petroleum ether 1:5) gave an inseparable mixture or **10** and **11**, 80 mg (72%). The respective NMR spectra were determined from the stereomeric mixture. **10-*anti*:** $^1$H NMR δ 7.89–7.46 (m, 5H), 4.99 (br s, 1H), 4.14 (q, *J* = 7 Hz, 3H), 3.66 (d, *J* = 8.5 Hz, 1H), 2.92–2.78 (m, 1H), 2.69 (dd, *J* = 15.5, 3.5 Hz, 1H), 2.21 (dd, *J* = 15.5, 9 Hz, 1H), 1.67 (br

s, 3H), 1.32 (d, $J$ = 7 Hz, 3H), 1.26 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR $\delta$ 172.0 (s), 139.1 (s), 137.5 (s), 133.4 (d), 128.8 (d, 2 × CH), 128.7 (d, 2 × CH), 121.1 (t), 75.8 (d), 60.5 (t), 39.0 (t), 30.1 (d), 21.8 (q), 18.8 (q), 14.2 (q). **11-*syn***: $^1$H NMR $\delta$ 7.89–7.46 (m, 5H), 4.98 (br s, 1H), 4.87 (br s, 1H), 4.15 (q, $J$ = 7 Hz, 3H), 3.86 (d, $J$ = 8 Hz, 1H), 2.93–2.78 (m, 1H), 2.63 (dd, $J$ = 17, 8.5 Hz, 1H), 1.68 (br s, 3H), 1.27 (t, $J$ = 7 Hz, 3H), 1.14 (d, $J$ = 6.5 Hz, 2H); $^{13}$C NMR $\delta$ 172.0 (s), 139.1 (s), 137.5 (s), 133.4 (d), 128.8 (d, 2 × CH), 128.7 (d, 2 × CH), 121.3 (t), 75.8 (d), 60.4 (t), 39.0 (t), 29.2 (d), 21.6 (q), 17.9 (q), 14.2 (q); MS of (**10** + **11**) $m/z$ 311 ($MH^+$, 76), 266 (45), 169 (100). Anal. Calcd for **10** + **11** $C_{16}H_{22}O_4S$: C, 61.91; H, 7.14. Found: C, 61.80; H, 7.41.

The above reaction was repeated under identical conditions in the presence of HMPA (0.5 mL in 0.5 mL of THF) added prior (5 min) to ethyl crotonate. Integration of the $^1$H NMR of the crude product showed a 14:86 ratio of **10**/**11**. Chromatographic purification gave 82 mg (73% of the above stereomeric mixture).

**Reactions of Methallyl Sulfone 9 with 1-Nitropropene.** The reactions were performed as shown above for ethyl crotonate. After 3–5 min the conversion was completed (TLC), and the reaction mixture was quenched and extracted as usual. The diastereomeric ratio was determined by integration of $^1$H NMR spectrum of the residue: **12-*anti*/13-*syn*** 1:4. Chromatography (petroleum ether/EtOAc 3:1) gave first **13** (59 mg) and then a mixture of **13** and **12** (24 mg), total yield 81%. In the presence of HMPA (added as shown for ethyl crotonate) the same stereomeric ratio was obtained in 79% total yield. The NMR spectra of **12** were determined by subtracting the signals of **13** in the mixtures of **12** and **13**.

**12-*anti***: $^1$H NMR $\delta$ 7.89–7.49 (m, 5H), 5.09 (br s, 1H), 4.99 (br s, 1H), 4.77 (dd, $J$ = 13, 4 Hz, 1H), 4.34 (dd, $J$ = 13, 8 Hz, 1H), 3.70 (d, $J$ = 8 Hz, 1H), 3.25–3.07 (m, 1H), 1.68 (br s, 3H), 1.40 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR $\delta$ 138.6 (s), 136.4 (s), 133.8 (d), 128.9 (d, 4 × CH), 121.7 (t), 79.2 (t), 73.5 (d), 32.4 (d), 22.2 (q), 16.5 (q).

**13-*syn***: mp 100 °C; $^1$H NMR $\delta$ 7.89–7.49 (m, 5H), 5.01 (dd, $J$ = 13, 5 Hz, 1H), 4.99 (br s, 1H), 4.84 (br s, 1H), 4.76 (dd, $J$ = 13, 8 Hz, 1H), 3.75 (d, 9.5 Hz, 1H), 3.24–3.08 (m, 1H), 1.68 (br s, 3H), 1.15 (d, $J$ = 7 Hz, 3H); $^{13}$C NMR $\delta$ 137.9 (s), 136.3 (s), 133.9 (d), 128.9 (d, 4 × CH), 122.2 (t), 78.9 (t), 73.2 (d), 31.2 (d), 20.9 (q), 15.9 (q); MS $m/z$ 284 ($MH^+$, 36), 142 (100), 125 (14), 95 (11). Anal. Calcd for $C_{13}H_{17}NO_4S$: C, 55.10; H, 6.05; N, 4.94. Found: C, 54.80; H, 5.95; N, 5.03.

**Base Equilibration of Cyclization Products.** The reaction mixture obtained from **1** and **3b** (for procedure see Table III) containing cyclized products **6b**, **7b**, and **8b** was cooled from −40 °C to −78 °C, and *n*-BuLi (0.15 mL, 1.52 M in hexane, 0.23 mmol) was added dropwise. After stirring for 2 h at the above temperature and quenching, workup as before and chromatography (EtOAc/$CH_2Cl_2$/petroleum ether 1:1:5) gave first **4b** (13 mg, 10%) and then **6b** (48 mg, 45%).

**Preparation of *cis*-Hydrindane 21.** Bromo sulfone **1** (100 mg, 0.36 mmol) was reacted with 1-nitrocyclohexene (51 mg, 0.4 mmol) under conditions and amounts shown above for reactions in Table II. After 2 h at −78 °C the reaction mixture was worked up as usual and the residue was chromatographed (EtOAc/petroleum ether, 1:3) to give **21** (61 mg, 53%): mp 127 °C (from EtOAc/petroleum ether); $^1$H NMR $\delta$ 7.96–7.54 (m, 5H), 5.38 (ddd, $J$ = 3, 2, 1 Hz, 1H), 5.35 (ddd, $J$ = 3, 2, 1 Hz, 1H), 3.83 (dq, $J$ = 9, 2 Hz, 1H), 3.43 (ddt, $J$ = 9, 5, 2 Hz, 1H), 2.62 (dq, $J$ = 15, 2 Hz, 1H), 2.52 (brd, $J$ = 15 Hz, 1H), 2.39 (dtd, $J$ = 15, 3, 2 Hz, 1H), 1.81–1.54 (m, 4H), 1.46 (ddd, $J$ = 15, 12, 3 Hz, 1H), 1.35–1.08 (m, 2H); $^{13}$C NMR $\delta$ 137.9 (s), 136.5 (s), 134.2 (d), 129.9 (d, 2 × CH), 129.2 (d, 2 × CH), 118.6 (t), 89.7 (s), 69.0 (d), 47.0 (t), 42.2 (d), 31.5 (dd), 24.1 (t), 20.9 (t), 19.6 (t); MS $m/z$ 339 ($MH_2O^+$, 34), 275 (100), 133 (54). Anal. Calcd for $C_{16}H_{19}NO_4S$: C, 59.97; H, 5.96; N, 4.36. Found: C, 59.90; H, 5.84; N, 4.59.

**Acknowledgment.** We are grateful to Dr. Hugo Gottlieb for help with the NMR spectra. Partial support of this research by a grant from the U.S.–Israel Binational Science Foundation is gratefully acknowledged.

**Supplementary Material Available:** Copies of $^{13}$C NMR spectra (20 pages). This material is available in libraries on microfiche, immediatley 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.