chromatography over silica gel with 10% ethyl acetate in hexane afforded 15 mg (37%) of enone **39b**: ^{1}H NMR ($CDCl_3$) δ 6.82–5.92 (m, 2 H), 5.45–4.89 (br m, 3 H), 3.96 (br m, 1 H), 3.68 (s, 3 H), 2.09 (s, 3 H), 0.88 (s, 9 H), 0.09 (s, 6 H); IR (film) 1735, 1670, 1630, 1250, 870, 735 cm^{-1}.

A 49-mg (0.09 mmol) sample of enone **39b** in 1 mL of methanol containing 34 mg (0.10 mmol) of $CeCl_3 \cdot 6H_2O$ was treated at room temperature with 3.6 mg (0.10 mmol) of sodium borohydride.[45] The reaction mixture was stirred at room temperature for 20 min, after which 6 drops of a saturated aqueous solution of ammonium chloride was added. The products were isolated with ethyl acetate in the usual manner to provide 49 mg (100%) of the C-15 epimeric alcohols **39c** and **39d**: ^{1}H NMR ($CDCl_3$) δ 5.42 (m, 4 H), 5.02 (br m, 1 H), 4.09 (br m, 1 H), 3.69 (s, 3 H), 0.88 (s, 9 H), 0.09 (s, 6 H), IR (film) 3500, 1735, 1250, 870, 735 cm^{-1}.

Treatment of the above 49-mg (0.09 mmol) sample of allylic alcohols **39c** and **39d** with 1 mL of acetic acid–water–THF (3:1:1) for 24 h at room temperature yielded on solvent evaporation a mixture of epimeric alcohols **40a** and **40b**. Separation of the mixture on silica gel with 2% methanol in methylene chloride afforded 10 mg of the less polar[19] 15β-isomer **40a**, 12 mg of the more polar[19] 15α-isomer **40b**, and 5 mg of a mixture of the α and β isomers (71% yield). α-Isomer **40b**: ^{1}H NMR ($CDCl_3$) δ 5.51–4.84 (br m, 5 H), 3.90 (br m, 2 H), 3.57 (s, 3 H), 2.00 (s, 3 H), 0.91 (br t, 3 H); IR (film) 3450, 1735, 1250 cm^{-1}. Treatment of the β-isomer **40a** (10 mg, 0.02 mmol) with 36 mg (0.4 mmol) of manganese dioxide in 0.5 mL of methylene chloride for 14 h generated the corresponding enone (8.5 mg).

A 6-mg (0.01 mmol) sample of diester **40b** was stirred at room temperature in 2.0 mL of 35% aqueous methanol containing 32 mg (0.23 mmol) of potassium carbonate. After 36 h, water was added, and the methanol was evaporated under reduced pressure. The aqueous solution was then acidified to pH 2–3 with cold 10% hydrochloric acid, and the product was isolated with ether in the usual manner to furnish quantitatively (5 mg) $PGF_{2\alpha}$ (**41**). This material was indistinguishable from an authentic sample of racemic $PGF_{2\alpha}$ that was kindly provided to us by Dr. J. Pike (The Upjohn Co.). The corresponding methyl ester, obtained by treatment of $PGF_{2\alpha}$ with diazomethane in ether and purified by filtration over silicic acid, was also identical in all respects with an authentic sample; ^{1}H NMR ($CDCl_3$) δ 5.48 (m, 4 H), 4.39–3.85 (br m, 2 H), 3.67 (s, 3 H), 0.90 (br t, 3 H); IR (film) 3300, 1735 cm^{-1}; mass spectrum, m/e 350 ($M^+ - H_2O$).

Acknowledgment. We thank Dr. W. Bartmann (Hoechst A.G.) for a sample of 11-deoxy-PGE_1, Dr. J. Pike (The Upjohn Co.) for a sample of $PGF_{2\alpha}$, and C. Bosso for the mass spectra. We are also indebted to Dr. J. L. Luche for helpful discussions and a referee for useful comments. Fellowship awards from the CNPq (to M.A.T. and E.B.) and SARSA (to E.B.) of Brasil and the CONACYT (to A.C.) of Mexico are gratefully acknowledged. This work was supported by the CNRS (ERA No. 478).

Registry No. **1**, 2161-40-2; **2**, 59807-39-5; **3**, 81424-02-4; **4**, 57337-65-2; **4** dihydroxy derivative, 81424-03-5; **5**, 74787-11-4; **6**, 57337-67-4; **7a**, 57337-68-5; **7b**, 57337-69-6; **8a**, 57337-70-9; **8b**, 61045-36-1; **8c**, 57378-32-2; **9**, 34603-80-0; **10**, 81424-04-6; **11a**, 81424-05-7; **11b**, 81424-06-8; **11c**, 81424-07-9; **12b**, 81424-08-0; **13**, 81424-09-1; **14a**, 75758-61-1; **14b**, 37517-79-6; **14b***, 13345-50-1; **15**, 81424-10-4; **15** (*endo*-methyl isomer), 81446-07-3; **16**, 81446-08-4; **16** diacetal derivative, 81424-11-5; **17** (isomer 1), 81424-12-6; **17** (isomer 2), 81446-09-5; **18a**, 81424-13-7; **18b**, 81424-14-8; **19**, 81424-15-9; **20a**, 81424-16-0; **20b**, 81424-17-1; **20c**, 81424-18-2; **21**, 62777-52-0; **22**, 81424-19-3; **23**, 81424-20-6; **24**, 81424-21-7; **25**, 81424-22-8; **26** (isomer 1), 81424-23-9; **26** (isomer 2), 81446-10-8; **27a**, 81424-24-0; **27b**, 81424-25-1; **28**, 81424-26-2; **29a**, 81424-27-3; **29a***, 81424-28-4; **29b**, 81424-29-5; **29b***, 81424-30-8; **29c**, 81424-31-9; **29c***, 78407-39-3; **30a**, 81424-32-0; **30a***, 81424-33-1; **30b**, 81424-34-2; **30b***, 81424-35-3; **32**, 81424-36-4; **33** (4α-butyl isomer), 81424-37-5; **33** (4β-butyl isomer), 81446-11-9; **34**, 81424-38-6; **35a**, 81424-39-7; **35b**, 81424-40-0; **36a**, 81424-41-1; **36b**, 81424-42-2; **36b** acetate, 81424-43-3; **36c**, 81424-44-4; **37a**, 81424-45-5; **37b**, 81424-46-6; **37c**, 81424-47-7; **37d**, 81424-48-8; **38a**, 81424-49-9; **38b**, 81424-50-2; **39a**, 81424-51-3; **39b**, 81424-52-4; **39c**, 81424-53-5; **39d**, 81424-54-6; **40e**, 81424-55-7; **40b**, 81424-56-8; **41**, 23518-25-4; **41** methyl ester, 57794-75-9; **ia***, 31753-19-2; **ib***, 36677-05-1; **iia***, 81424-57-9; **iib***, 81424-58-0; ethyl 7-iodoheptanoate, 51100-70-0; ethyl 7-iodo-5-heptynoate, 81424-59-1; 2-methoxypropene, 116-11-0; (methoxymethyl)triphenylphosphonium chloride, 4009-98-7; (4-carboxybutyl)triphenylphosphonium bromide, 17814-85-6; dimethyl (2-oxoheptyl)phosphonate, 36969-89-8.

Preparation of Ring-Substituted (Arylsulfonyl)cyclopropanes and (Arylsulfonyl)bicyclobutanes from γ,δ-Epoxy Sulfones

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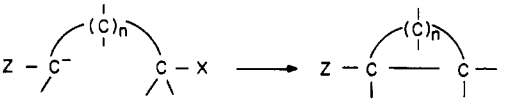
Treatment of γ,δ-epoxy sulfones **2** with *n*-butyllithium provides 1-(hydroxyalkyl)-2-(arylsulfonyl)cyclopropanes (**3**). Dehydration of the latter, when applicable, yields 1-alkenyl-2-(arylsulfonyl)cyclopropanes (**5**) which can be epoxidized and converted by a second base treatment into 2-(hydroxyalkyl)-1-(arylsulfonyl)bicyclo[1.1.0]butanes (**7**). An alternative route to bicyclobutanes consists of treating the epoxy sulfones **2** consecutively with *n*-butyllithium, methanesulfonyl chloride, and *n*-butyllithium. 1-(Arylsulfonyl)bicyclo[1.1.0]butanes (**9**), devoid of the hydroxyl groups in the side chain, are obtained in ca. 50% overall yield.

Intramolecular nucleophilic substitution at a remote center by a stabilized carbanion is a method that has been extensively utilized for carbocyclic ring formation. Halogens, sulfonate esters, and epoxidic oxygens have been most often used as the leaving group X (Scheme I), while the carbanion-stabilizing group Z could be a carbonyl, nitrile, ester, sulfone, or other electron-withdrawing group.[1,2]

Scheme I



When the leaving group X is an epoxidic oxygen, some ambiguity may result from the presence of two sites where displacement by the anion can occur.[2,3] The actual re-

(1) (a) Mathieu, J.; Weil-Raynal, J. "Formation of C–C Bonds"; Georg Thieme Verlag: Stuttgart, 1975; Vol. II, pp 2–4, 106–10, 134. (b) Warnhoff, E. W.; Srinivasan, V. *Can. J. Chem.* **1977**, *55*, 1629–34 and references cited therein.

(2) (a) Stork, G.; Cama, L. D.; Coulson, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 5268–70. (b) Stork, G.; Cohen, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 5270–2.

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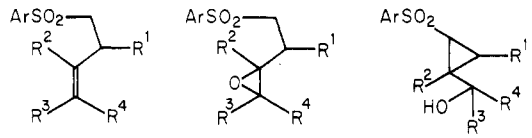
Chart I[a]



1 2 3

[a] a, $R^1 = R^2 = R^3 = R^4 = H$ (Ar = Ph); b, $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$ (Ar = Ph, *p*-tolyl); c, $R^1 = R^2 = R^4 = H$, $R^3 = CH(CH_3)_2$ (Ar = Ph, *p*-tolyl); d, $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$ (Ar = Ph, *p*-tolyl); e, $R^1 = R^2 = H$, $R^3,R^4 = (CH_2)_4$ (Ar = Ph); f, $R^1 = R^2 = H$, $R^3,R^4 = (CH_2)_5$ (Ar = Ph); g, $R^1 = R^4 = H$, $R^2,R^3 = (CH_2)_4$ (Ar = Ph); h, $R^2 = R^3 = H$; $R^1,R^4 = (CH_2)_3$ (Ar = Ph).

action site is eventually determined, though not always in a definite way, by the restrictive requirement that the attacking carbanion, the carbon undergoing the nucleophilic displacement, and the departing oxygen be collinear.[1b,2b,3,4]

When the epoxide function is located at a γ,δ-position relative to group Z, backside collinearity may be readily attained with the γ-carbon to oxygen bond but is practically impossible to achieve with the δ bond. As a result, cyclopropane derivatives are formed exclusively in such cases, the alternative cyclobutanes not being detected. The method could thus be applied to the preparation of cyclopropane derivatives from γ,δ-epoxyalkylated ketones,[5] nitriles,[2b] sulfones,[6,7] esters,[8,9] and other functional groups.

This paper gives a detailed account of our investigations regarding the base-induced reactions of γ,δ-epoxy sulfones as applied to the preparation of cyclopropane and bicyclobutane derivatives.[6,10] The former compounds were prepared in view of their usefulness as synthetic intermediates in the construction of condensed bi- and polycyclic systems via divinylcyclopropanes.[11] The two complementary preparations of bicyclobutanes, on the other hand, represent facile routes to these highly strained molecules and might provide access to novel condensed and bridged systems comprising this unit. One such system is described further below.

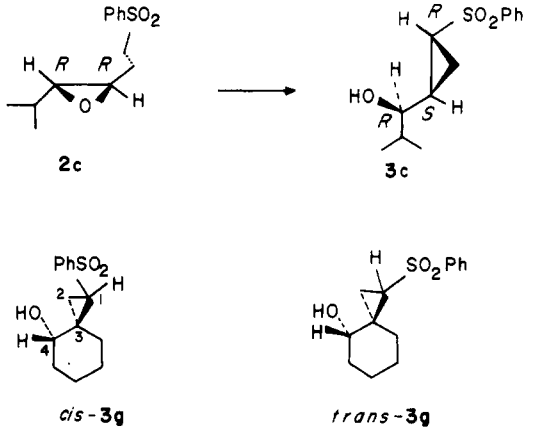
Results and Discussion

γ,δ-Unsaturated sulfones (**1**; Chart I) were prepared by coupling of [(arylsulfonyl)methyl]magnesium bromide with allylic halides. Epoxidation with *m*-chloroperbenzoic acid (MCPBA) provided the γ,δ-epoxy sulfones **2**. A unique racemic epoxide was obtained in all cases, except for **2h**, where a cis and a trans epoxide were obtained in a ratio of ca. 3:1, respectively.

Treatment of epoxides **2** in tetrahydrofuran (THF) with *n*-butyllithium (BuLi) at −15 or 0 °C provided the 1-(hydroxyalkyl)-2-(arylsulfonyl)cyclopropanes **3**, usually in 80–95% yields. Epoxide *cis*-**2h** failed, however, to react because backside collinearity was impossible to achieve in this case.

The geometry of the hydroxyalkyl and arylsulfonyl groups in **3** was specifically trans in all cases where R^2 = H. Backside collinearity does not preclude, in fact, the freedom of the arylsulfonyl group to assume a less congested transoid transition geometry leading to a trans compound. However, when $R^2 \neq H$ (**2b,g**), both cis and trans transition geometries become almost equally congested, and the two possible geometrical isomers of **3** are formed.

Scheme II



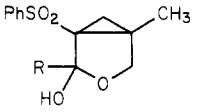
2c **3c**

cis-**3g** *trans*-**3g**

On consideration of the possible formation of two **3** diastereoisomers when $R^3 \neq R^4$ (**3c,g,h**), backside collinearity determines that only one of them be produced from each epoxide **2**. It can, indeed, be seen (Scheme II) that the trans epoxide **2c**, for example, would produce (*RS,SR,RS*)-**3c** only and that the hydroxyl group in **3g** can only assume a trans position relative to the newly formed 1,3-bond. A unique diastereomer was, indeed, obtained for **3c,h** and each of the geometrical isomers of **3g**.

The trans configuration of cyclopropanes **3**, when R^2 = H, was demonstrated by their conversion into divinylcyclopropane derivatives and by the ready interaction of the two vinyl groups.[11] Unless total inversion had occurred during hydroxyalkylation α to the sulfone, the initial configuration must have been trans.

Further indication as to the relative geometry of substituents on the cyclopropane ring was gained from ^1H NMR spectra of compounds **3**. Thus, the aliphatic methyl signals in the two isomeric compounds **3b** (Ar = *p*-tolyl) appeared at δ 1.28 and 1.48. Treatment of the propionate ester of the second isomer with BuLi produced **4b** in which



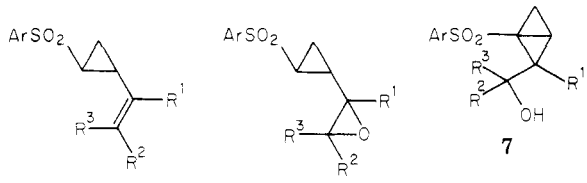
4a, R = Me
b, R = Et

the *cis*-methyl signal appeared at δ 1.67. This allows one to conclude that a group cis to the arylsulfonyl was relatively considerably deshielded. This observation was later confirmed in other compounds, particularly bicyclobutanes, and could thus be used as a diagnostic tool to determine the relative configuration in still other compounds. Thus, the chemical shift of the CHOH proton in **3g** is δ 3.55 for the less abundant isomer and δ 4.39 for the more abundant one. A configuration of *cis*-CHOH relative to the phenylsulfonyl group on the common cyclopropane ring was therefore assigned to the latter isomer (Scheme II).

Several compounds **3** carrying a secondary or tertiary hydroxyl group have been dehydrated with *p*-toluenesulfonic acid in benzene to provide the vinylic derivatives **5** in 65–85% yields. This constitutes the first step in the

(3) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–6.
(4) Lallemand, J. Y.; Onaga, M. *Tetrahedron Lett.* **1975**, 585–8.
(5) Gaoni, Y. *Isr. J. Chem.* **1971**, *9*, 63–9; *Tetrahedron* **1972**, *28*, 5525–31; 5533–41.
(6) Gaoni, Y. *Tetrahedron Lett.* **1976**, 503–6.
(7) (a) Corbel, B; Durst, T. *J. Org. Chem.* **1976**, *41*, 3648–50. (b) Corbel, B.; Decesare, J. M.; Durst, T. *Can. J. Chem.* **1978**, *56*, 505–11. (c) Decesare, J. M.; Corbel, B.; Durst, T.; Blount, J. F. *Can. J. Chem.* **1981**, *59*, 1415–24.
(8) Babler, J. H.; Tortorello, A. J. *J. Org. Chem.* **1976**, *41*, 885–7.
(9) Ficini, J.; D'Angelo, J. *Tetrahedron Lett.* **1976**, 2441–4.
(10) Gaoni, Y. *Tetrahedron Lett.* **1981**, 4339–40.
(11) To be described in a forthcoming publication from this laboratory.

Chart II[a]



5 6 7

[a] a, $R^2 = R^3 = H$, $R^1 = CH_3$ (Ar = Ph, *p*-tolyl); b, $R^1 = H$, $R^2 = R^3 = CH_3$ (Ar = Ph, *p*-tolyl); c, $R^3 = H$, $R^1,R^2 = (CH_2)_3$ (Ar = Ph).

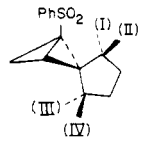


Figure 1. Configurational assignments for the **7c** isomers.

conversion of **3** to divinylcyclopropanes[11] or to bicyclobutanes **7** via epoxides **6** (Chart II). Compounds **5** are indeed, again, γ,δ-unsaturated sulfones on which the above sequence of reactions could be repeated.

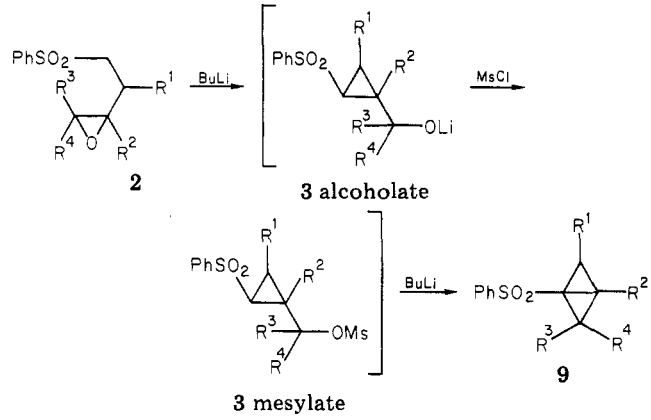
Epoxidation of **5** with MCPBA produced epoxides **6** as diastereomeric mixtures which were difficultly separable by chromatography. In particular, the sharp melting point of a 1:1 mixture of the **6c** isomers and the appearance of their epoxidic protons as sharp singlets separated by 11.7 Hz could make this mixture appear as a unique compound.

Epoxides **6** were submitted to the action of BuLi as an unseparated or partly enriched diastereomeric mixture, noticing that by virtue of a backside collinear attack each isomer would produce one single bicyclobutane **7**, as has been the case for the conversion of **2** to **3**. Two **7a** isomers were obtained in equal amounts and in a low 24% total yield from a 1:1 mixture of the **6a** isomers. These could now be readily separated and characterized. In the case of **6b**, however, only one **7b** isomer was isolated and shown by ^1H NMR to be the 2-*exo*-isopropyl derivative. One **6b** isomer was recovered from the reaction mixture, and when submitted separately to the action of BuLi it was again recovered practically unchanged. It was assumed to be the isomer that would lead to the highly hindered 2-*endo*-isopropyl compound **7b**.

Epoxides **6c** were exceptional in their behavior toward the action of BuLi in that their mixture produced four different **7c** isomers, identified as isomers I–IV according to their order of elution from chromatography. The configurational assignments are shown in Figure 1, the position of the hydroxyl being indicated by the numeral of the corresponding isomer. These assignments are based on the chemical shifts of the CHOH proton (δ 4.12 and 4.48 for I and II, cis to the phenylsulfonyl group on the common cyclopropane ring, and δ 3.69 and 3.75 for III and IV) and on the relative polarity, the more hindered *syn*-I being expected to be less polar than *anti*-II, the same for III and IV.

Epoxides **6c** could be separated by fractional crystallization into one pure isomer (mp 104 °C) and one enriched isomer (ratio of ca. 9:2). The first isomer was then found to produce exclusively **7c** isomers II and III and the second mainly I and IV. It is apparent that only isomers II and IV can be produced here by a backside attack on the two diastereomeric oxygens. It is, therefore, necessary to invoke a different mechanism in order to account for the formation of I and III. We propose that in this case an S_N1-type reaction is taking place, with dissociation of the γ-C–O bond prior to C–C bond formation. This would still

Scheme III[a]

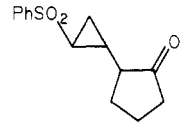


2 3 alcoholate 3 mesylate 9

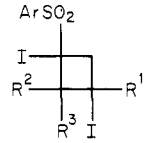
[a] a, $R^1 = R^2 = R^3 = R^4 = H$; b, $R^1 = R^3 = R^4 = H$, $R^2 = CH_3$; c, $R^1 = R^2 = R^3 = H$, $R^4 = CH(CH_3)_2$; d, $R^1 = R^2 = H$, $R^3 = R^4 = CH_3$; e, $R^2 = R^4 = H$; $R^1,R^3 = (CH_2)_3$; f, $R^3 = R^4 = H$, $R^1,R^2 = (CH_2)_4$.

produce the same respective **7c** isomers from each **6c** epoxide.

The assumption of an S_N1-type reaction is strongly corroborated here by the observation of the facile rearrangement of the **6c** epoxides into ketone **8**. This not only



8



10a, $R^1 = R^2 = H$; $R^3 = C(OH)(CH_3)_2$
b, $R^1 = H$; $R^2,R^3 = CH_2CH_2CH_2CHOH$
c, $R^1 = R^2 = R^3 = H$
d, $R^2 = R^3 = H$; $R^1 = CH_3$
e, $R^1 = R^3 = H$; $R^2 = CH(CH_3)_2$
f, $R^1 = H$; $R^2 = R^3 = CH_3$

occurs very readily by acid catalysis but also takes place spontaneously when both **6c** isomers are kept at room temperature for a few weeks; crystalline **6c** then partly melts, and ketone **8** may be obtained by chromatographic separation. Alternatively, short treatment of **6c** with *p*-toluenesulfonic acid in dichloromethane–benzene produces **8** in a minimum 68% yield. The reaction probably proceeds by protonation on oxygen, opening of the oxirane ring with generation of a cyclopropyl carbinyl cation, and formation of an enol by proton loss. It is assumed that during the base-induced conversion of **6c** to **7c**, a lithium cation may similarly assist in the opening of the oxirane ring, thus making possible a front-side attack and formation of the abnormal **7c** isomers I and III.

A simpler, more direct route to bicyclobutanes proceeds directly from epoxides **2**. It consists of treating the lithium alcoholate of **3** in situ with methanesulfonyl chloride, followed by base treatment of the resulting sulfonate ester (Scheme III). The sequence can be easily carried out in one reaction vessel, without isolation of the intermediates, at a temperature of 0 °C and in 10–15 min total reaction time. Bicyclobutanes **9**, devoid here of the hydroxyl group, are obtained usually in ca. 50% overall yield. Sulfone **9f**, representing a novel tricyclooctane system, was obtained from **2g** in 40% overall yield.

It is noteworthy that in the case of **2d** (Ar = Ph), where the intermediate methanesulfonate (Scheme III) would be tertiary, elimination was only occasionally observed and

only to a small extent (5–10%). However, when applied to **2e**, the sequence of reactions led to the exclusive formation of **5c**, with no bicyclobutane being detected.

The intermediate alcohols **3** or their sulfonate esters could, of course, be alternatively used to prepare **9**. Thus, both **3b** mesylates were reactive in producing **9b** in ca. 80% yield. It is apparent that in the case of the *cis*-**3b** isomer, as well as in the case of *cis*-**3g**, inversion of configuration of the α-sulfonyl carbanion[12] has to take place before displacement on the sulfonate ester can occur. A 91% yield of **9c** (*p*-tolyl instead of phenyl sulfone) was obtained from **3c** tosylate. The high yield may be ascribed to the fact that the unique **3c** isomer at hand (Scheme II) is the one that would place the isopropyl group in an exo position in **9c**, and thus greatly facilitate the reaction.

All of the bicyclobutanes **9** were obtained as stable solids or as stable, distillable liquids (**9c,d**). Liquid bicyclobutanes **7** were less stable, and particularly the **7c** isomers. All **7** and **9** compounds were easily identified by their characteristic ^{1}H NMR spectra and by their property to readily absorb iodine in solution[13] or iodine vapor on TLC plates. Iodine addition products **10** were prepared from several of compounds **7** and **9**.

Some characteristics of the ^{1}H NMR spectra of products **7** and **9** are the very small or totally absent geminal coupling of the exo and endo protons (J values of 0–2 Hz), the deshielding of the exo protons, particularly the bridgehead proton, and the shielding of the endo protons. Replacement of the bridgehead proton by deuterium, particularly in all four **7c** isomers, confirmed the endo–exo assignments by observing that for vicinal protons on a cyclopropane ring $J_{cis} > J_{trans}$.

Application of the above method, which consists of a double intramolecular alkylation of a sulfone by an epoxide function, to the preparation of novel condensed or bridged, strained bicyclic systems is being further studied.

Experimental Section

General Procedures. Melting points were taken on a Fisher-Johns apparatus and were not corrected. Infrared spectra were measured with a Perkin-Elmer Infracord 137 or 457A grating spectrometer. Proton NMR spectra were measured in deuteriochloroform with a Varian A-60 spectrometer. Fourier transform ^{1}H spectra were determined on a Varian FT-80A spectrometer and are denoted by "(80)". All chemical shifts are reported in δ units downfield from internal Me_4Si, and the J values are given in hertz. Mass spectra were determined with an Atlas MAT 731 or MAT CH4 spectrometer. TLC was done on Merck Kieselgel 60-F254 precoated aluminum plates. The silica gel for column chromatography was Merck Kieselgel 60 (70–230 mesh).

THF was dried by distillation from lithium aluminum hydride or from sodium diphenyl ketyl. Commercial BuLi in hexane was titrated with diphenylacetic acid.[14] All reactions with BuLi were carried out under argon atmosphere by using syringe and septum techniques for handling of air-sensitive reagents.[15]

Difficultly distillable liquid compounds were obtained chromatographically and spectroscopically pure and were submitted to elemental analysis as their next solid derivatives or as their aromatic homologues. Elemental analyses were performed by Mr. R. Heller of the Weizmann Institute of Science, Microanalytical Laboratory.

Preparation of γ,δ-Unsaturated Sulfones 1. A solution of phenyl or *p*-tolyl methyl sulfone (0.10 mol) in benzene (100 mL) was introduced rapidly at room temperature into a stirred solution of ethylmagnesium bromide in THF [prepared from magnesium (3 g, 0.123 mol) and ethyl bromide (15 g, 0.138 mol) in 60 mL of solvent; the use of ether in earlier preparations resulted in inhomogeneous mixtures, and yields reported herein for some of the products are probably minimum yields]. After 10 min, the solution was brought rapidly into boiling with a preheated oil bath, maintained for 3 min at reflux, and cooled back to ca. 20 °C with ice–water. A solution of an allylic halide (0.09 mol) dissolved in an equal volume of benzene was then introduced rapidly. A slight exothermal effect was sometimes observed at this stage. Addition of cuprous chloride (0.5 g, 0.05 mol) considerably accelerated this effect, and the temperature rose generally to 40–45 °C. The reaction was warmed for 1–2 h at 50–60 °C, cooled, and poured on ice and 5% hydrochloric acid. An extractive workup with ether yielded a crude product which usually contained a few percent of a dialkylated sulfone (less polar spot than major product on TLC). Chromatography on silica gel (100–150 g; elution with hexane–ether, 4:1 to 3:1) separated the di- from the monoalkylated sulfone.

4-(Phenylsulfonyl)-1-butene (**1a**): bp 160 °C (bath temperature; 0.13 kPa); 70% yield relative to allyl bromide; NMR (80) δ 2.3–2.6 (m, 2), 3.1–3.3 (m, 2), 4.9–5.2 (m, 2), 5.5–6.0 (m, 1), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1310, 1140, 1080, 995, 925 cm^{-1}. Anal. ($C_{10}H_{12}O_2S$) C, H.

2-Methyl-4-(phenylsulfonyl)-1-butene (**1b**, Ar = Ph): mp 44–45 °C (pentane); yield 90%; NMR (80) δ 1.68 (s, Me), 2.3–2.5 (m, 2), 3.1–3.3 (m, 2), 4.65 and 4.76 (2 br s, 2, methene), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1310, 1150, 1085, 900 cm^{-1}. Anal. ($C_{11}H_{14}O_2S$) C, H.

2-Methyl-4-(*p*-tolylsulfonyl)-1-butene (**1b**, Ar = *p*-tolyl): mp 31–32 °C (pentane); yield 76%; NMR δ 1.67 (br s, Me), 2.35 (m, 2), 2.42 (s, Me), 3.20 (m, 2), 4.65 and 4.77 (2 br s, methene), 7.37 and 7.82 (AB-like, 4); IR ($CHCl_3$) 1602, 1300, 1142, 1086, 896 cm^{-1}; mass spectrum, m/e 244 (M^+), 157, 140, 139, 105, 92, 91. Anal. ($C_{12}H_{16}O_2S$) C, H, S.

2-Methyl-6-(phenylsulfonyl)-3-hexene (**1c**, Ar = Ph): yield 74%; NMR δ 1.92 (d, J = 7, 2 Me), 2.0–2.6 (m, 2), 3.0–3.3 (m, 2), 5.40 (m, 2), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1290, 1130, 1084 cm^{-1}.

2-Methyl-6-(*p*-tolylsulfonyl)-3-hexene (**1c**, Ar *p*-tolyl): yield 59%; NMR δ 1.92 (d, J = 7, 2 Me), 2.0–2.6 (m, 2), 2.46 (s, Me), 3.0–3.3 (m, 2), 5.40 (m, 2), 7.40 and 7.85 (Ab-like, 4); IR ($CHCl_3$) 1310, 1250, 1090 cm^{-1}.

2-Methyl-5-(phenylsulfonyl)-2-pentene (**1d**, Ar = Ph): yield 75%; NMR δ 1.53 (br s, Me), 1.62 (br s, Me), 2.1–2.7 (m, 2), 2.95–3.3 (m, 2), 5.02 (br t, 1), 7.45–8.1 (m, 5); IR ($CHCl_3$) 1310, 1150, 1088 cm^{-1}.

2-Methyl-5-(*p*-tolylsulfonyl)-2-pentene (**1d**, Ar = *p*-tolyl): yield 61% NMR δ 1.53 (br s, Me), 1.61 (br s, Me), 2.36 (m, 2), 2.43 (s, Me), 3.08 (m, 2), 4.98 (t, 1), 7.37 and 7.82 (AB-like, 4); IR (neat) 1290, 1140, 1080 cm^{-1}.

[3-(Phenylsulfonyl)propylidene]cyclopentane (**1e**): mp 30–31 °C (pentane); yield 68%; NMR δ 1.4–2.7 (m, 10), 3.0–3.3 (m, 2), 4.95–5.35 (m, 1), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1290, 1150, 1090 cm^{-1}. Anal. ($C_{14}H_{18}O_2S$) C, H.

[3-(Phenylsulfonyl)propylidene]cyclohexane (**1f**): yield 71%; NMR δ 1.35–2.25 (m, 10), 2.25–2.65 (m, 2), 2.95–3.30 (m, 2), 4.96 (br t, 1), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1310, 1150, 1090 cm^{-1}.

1-[2-(Phenylsulfonyl)ethyl]-1-cyclohexene (**1g**): yield 80%; NMR (80) δ 1.4–1.95 (m, 8), 2.2–2.45 (m, 2), 3.1–3.3 (m, 2), 5.38 (br s, 1), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1310, 1145, 1085 cm^{-1}; mass spectrum, m/e 250 (M^+), 143, 108, 95, 94, 93, 91.

3-[(Phenylsulfonyl)methyl]-1-cyclohexene (**1h**): yield 46%; NMR (80) δ 1.3–2.0 (m, 6), 2.83 (br, 1), 3.08 (d, 2), 5.64 (br AB q, 2, $J \approx 12$), 7.55–8.0 (m, 5); IR ($CHCl_3$) 1315, 1310, 1140, 1086 cm^{-1}; mass spectrum, m/e 236 (M^+), 143, 95, 94.

Preparation of Epoxides 2. Solid MCPBA (1.1 molar equiv of active peracid) was added in portions to a solution of sulfone **1** in dichloromethane (200 mL/0.05 mol of sulfone). Exothermal reactions were controlled by slight external cooling. The reaction time depended on the degree of substitution of the ethylenic bond. When all starting material was consumed (TLC monitoring), the reaction mixture was cooled in ice, and the *m*-chlorobenzoic acid was filtered. The filtrate was washed with sodium sulfite and sodium carbonate solutions and then with water and dried. Crude solid epoxides were purified by recrystallization. Others were chromatographed on 10–15 times by weight of silica gel, with ether–hexane mixtures as eluents.

(12) Ratajczak, A.; Anet, F. A. L.; Cram, D. J. *J. Am. Chem. Soc.* **1976**, *89*, 2072–7.
(13) Wiberg, K. B. *Adv. Alicyclic Chem.* **1968**, *2*, 185–254.
(14) Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1976**, *41*, 1879–80.
(15) See: Kramer, G. W.; Levy, A. B.; Mark Midland, M. In "Organic Syntheses via Boranes"; by Brown, H. C.; Wiley: New York, 1975; Chapter 9.

1,2-Epoxy-4-(phenylsulfonyl)butane (**2a**): mp 49–50 °C (ether–hexane); yield 89%; NMR (80) δ 1.7–3.4 (m, 7), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1310, 1140, 1085 cm^{-1}. Anal. ($C_{10}H_{12}O_3S$) C, H.

1,2-Epoxy-2-methyl-4-(phenylsulfonyl)butane (**2b**, Ar = Ph): mp 47–48 °C (ether–pentane); NMR (80) δ 1.29 (s, Me), 1.9–2.1 (m, 2), 2.59 (s, 2, C_1 H), 3.1–3.3 (m, 2), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1310, 1145, 985 cm^{-1}; mass spectrum, *m/e* 85, 84 ($M^+ - PhSO_2H$), 83. Anal. ($C_{11}H_{14}O_3S$) C, H.

1,2-Epoxy-2-methyl-4-(*p*-tolylsulfonyl)butane (**2b**, Ar = *p*-tolyl): mp 55–56 °C (ether–hexane); yield 89%; NMR δ 1.30 (s, Me), 2.0 (m, 2), 2.45 (s, Me), 2.60 (s, 2, C_1 H), 3.15 (m, 2), 7.4 and 7.8 (AB-like, 4); IR ($CHCl_3$) 1295, 1145 cm^{-1}; mass spectrum, *m/e* 240 (M^+), 210, 157, 140, 139, 91, 84 ($M^+ - C_7H_7SO_2H$). Anal. ($C_{12}H_{16}O_3S$) C, H, S.

3,4-Epoxy-2-methyl-6-(phenylsulfonyl)hexane (**2c**, Ar = Ph): yield 94%; NMR δ 1.90 (d, Me), 1.95 (d, Me), 1.2–2.3 (m, 3), 2.48 (dd, 1), 2.84 (m, 1), 3.25 (t, 2), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1307, 1145 cm^{-1}.

3,4-Epoxy-2-methyl-6-(*p*-tolylsulfonyl)hexane (**2c**, Ar = *p*-tolyl): yield 94%; NMR δ 1.90 (d, Me), 1.95 (d, Me), 1.2–2.2 (m, 3, C_2 H and C_5 H), 2.45 (s, Me), 2.50 (dd, 1, C_3 H), 2.83 (m, 1, C_4 H), 3.21 (t, 2, C_6 H), 7.40 and 7.85 (AB-like, 4); IR ($CHCl_3$) 1310, 1150 cm^{-1}; mass spectrum, *m/e* 197 ($M^+ - C_4H_7O$), 157, 155, 139, 112, 97, 92 ($M^+ - C_7H_7SO_2H$), 91.

2,3-Epoxy-2-methyl-5-(phenylsulfonyl)pentane (**2d**, Ar = Ph): yield 86%; NMR δ 1.20 (s, Me), 1.26 (s, Me), 1.6–2.4 (m, 2, C_4 H), 2.79 (dd, 1, J^1 = 5.5, J^2 = 7.5, C_3 H), 3.26 (t, 2, J = 8, C_5 H), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1300, 1140 cm^{-1}; mass spectrum, *m/e* 183 ($M^+ - C_3H_5O$), 98 ($M^+ - PhSO_2H$).

2,3-Epoxy-2-methyl-5-(*p*-tolylsulfonyl)pentane (**2d**, Ar = *p*-tolyl): mp 43–44 °C (pentane–ether); yield 81%; NMR δ 1.21 (s, Me), 1.26 (s, Me), 1.7–2.2 (m, 2, C_4 H), 2.45 (s, Me), 2.79 (dd, 1, J^1 = 5.5, J^2 = 7.0, C_3 H), 3.27 (t, 2, J = 8, C_5 H), 7.37 and 7.83 (AB-like, 4); IR ($CHCl_3$) 1300, 1140 cm^{-1}; mass spectrum, *m/e* 254 (M^+), 197 ($M^+ - C_3H_5O$), 98 ($M^+ - C_7H_7SO_2H$). Anal. ($C_{13}H_{18}O_3S$) C, H.

2-[(2-Phenylsulfonyl)ethyl]-1-oxaspiro[2.4]heptane (**2e**); mp 62–63 °C (benzene–hexane); yield 94%; NMR δ 1.5–2.0 (m, 8), 2.8–3.1 (m, 3), 3.3–3.65 (m, 2), 7.5–8.1 (m, 5); IR (KBr) 1295, 1150, 1090 cm^{-1}. Anal. ($C_{14}H_{18}O_3S$) C, H.

2-[(2-Phenylsulfonyl)ethyl]-1-oxaspiro[2.5]octane (**2f**): yield 81%; NMR δ 1.50 (br s, 10), 1.65–2.3 (m, 2), 2.78 (dd, 1 J^1 = 5.5, J^2 = 7.0), 3.30 (t, 2, J = 7.5), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1300, 1142, 1083 cm^{-1}.

1,2-Epoxy-1-[2-(phenylsulfonyl)ethyl]cyclohexane (**2g**): yield 90%; NMR (80) δ 1.2–2.1 (m, 10), 2.9–3.3 (m, 3), 7.55–8.0 (m, 5); IR ($CHCl_3$) 1314, 1301, 1150, 1086 cm^{-1}; mass spectrum, *m/e* 124 ($M^+ - PhSO_2H$), 110, 95, 94.

***cis*- and *trans*-2h.** The crude reaction product was chromatographed on silica gel (30 times by weight; elution with hexane–ether, 3:1). The ratio of the first-eluted, liquid cis epoxide to the solid trans epoxide was ca. 3:1 (total yield 82%).

cis-1,2-Epoxy-3-[(phenylsulfonyl)methyl]cyclohexane (*cis*-**2h**): NMR (80) δ 1.2–2.9 (m, 6), 2.62 (br t, 1), 2.9–3.6 (m, 4), 7.55–8.0 (m, 5); IR ($CHCl_3$) 1315, 1300, 1145, 1084 cm^{-1}; mass spectrum, *m/e* 143, 110 ($M^+ - PhSO_2H$), 95, 94, 93, 91.

trans-1,2-Epoxy-3-[(phenylsulfonyl)methyl]cyclohexane (*trans*-**2h**): mp 88–89 °C (hexane); NMR (80) δ 0.9–2.1 (m, 6), 2.42 (br t, 1), 3.0–3.3 (m, 4), 7.5–8.0 (m, 5); mass spectrum, *m/e* 143, 110 ($M^+ - PhSO_2H$), 95, 94, 93, 91. Anal. ($C_{13}H_{16}O_3S$) C, H.

Preparation of Cyclopropanes 3. A solution of BuLi in hexane (1.1–1.3 molar equiv) was added during 0.25 h to a stirred solution of **2** in THF (2.5 mL/mmol of **2**) cooled to −15 °C (ice–salt bath). Stirring was continued for 0.5 h at that temperature and for 0.3 h at room temperature. Water was added, and most of the THF was evaporated at reduced pressure. An extractive work up with ether provided a crude product which was usually purified by chromatography on silica gel (10 times by weight of product), followed by crystallization. In later experiments, reactions were carried out at 0 °C and for shorter periods of time (TLC monitoring).

trans-1-(Hydroxymethyl)-2-(phenylsulfonyl)cyclopropane (**3a**): yield 72%; NMR (80) δ 0.92–1.2 (m, 1, C_3 H trans to $PhSO_2$), 1.30–1.55 (m, 1, C_3 H cis to $PhSO_2$), 1.82–2.22 (m, 1, C_1 H; most highly split ring proton), 2.26 (br, 1, OH), 2.35–2.56 (m, 1, C_2 H), 3.31–3.80 (br m, 2, appears as a d AB q upon addition of D_2O, $J_{AB} \approx 12$, J_{AX} = 5.1, J_{BX} = 6.1, $\Delta\nu \approx 23$ Hz, CH_2OH), 7.5–8.0 (m, 5); IR ($CHCl_3$) 3430 (br), 1305, 1145, 1087 cm^{-1}; mass spectrum, *m/e* 212 (M^+), 169, 143, 142, 125, 124, 94, 91. 2,4-Dinitrobenzoate of **3a**, mp 147–148 °C (ethanol). Anal. ($C_{17}H_{14}N_2O_8S$) C, H.

The methanesulfonate of **3a** was obtained directly by quenching the above reaction with methanesulfonyl chloride (1 molar equiv): 72% yield; NMR (80) δ 1.04–1.29 (m, 1, C_3 H), 1.51–1.75 (m, 1, C_3 H), 1.95–2.29 (m, 1, C_1 H), 2.46–2.70 (m, 1, C_2 H), 2.94 (s, Me), 4.14 (d AB q, 2, J_{AB} = 11.2, J_{AX} = 5.9, J_{BX} = 7.4, $\Delta\nu \approx 33$ Hz, CH_2OMs); IR ($CHCl_3$) 1345, 1315, 1170, 1145, 1090, 955 cm^{-1}; mass spectrum, *m/e* 290 (M^+), 195, 149, 148, 125, 123, 122, 121, 104, 97, 91.

***cis*- and *trans*-3b (Ar = Ph).** The crude reaction product was chromatographed on 50 times its weight of silica gel (elution with dichloromethane–ether, 7:3). A total 40% yield of two isomeric alcohols was obtained in a ratio of ca. 1:1.

r-1-(Hydroxymethyl)-1-methyl-*c*-2-(phenylsulfonyl)cyclopropane (*cis*-**3b**, Ar = Ph): NMR (80) δ 1.15 (dd, 1, J^1 = 5.5, J^2 = 8.2, C_3 *t*-H), 1.28 (s, Me), 1.59 (t, 1, J = 5.5, C_3 *c*-H), 2.33 (dd, 1, J^1 = 5.6, J^2 = 8.2, C_2 H), 2.45 (br t, OH), 3.98 (d, 2, J = 6.8, s with added D_2O, CH_2OH), 7.55–8.0 (m, 5); IR ($CHCl_3$) 3500 (br), 1300, 1140, 1085, 1025 cm^{-1}; mass spectrum, *m/e* (relative intensity) 226 (M^+, <1), 169, 143, 125, 91, 84.

r-1-(Hydroxymethyl)-1-methyl-*t*-2-(phenylsulfonyl)cyclopropane (*trans*-**3b**, Ar = Ph): NMR (80) δ 1.2–1.5 (m, 2, C_3 H), 1.48 (s, Me), 2.32 (br, OH), 2.48 (dd, 1, J^1 = 5.6, J^2 = 8.2, C_2 H), 3.40 (AB q, 2, J_{AB} = 10.3, $\Delta\nu \approx 15$ Hz, CH_2OH), 7.5–8.0 (m, 5); IR ($CHCl_3$) 3400 (br), 1305, 1145, 1085 cm^{-1}; mass spectrum, *m/e* (relative intensity) 226 (M^+, <1), 169, 143, 125, 91, 84.

The **3b** methanesulfonates (Ar = Ph) were prepared from a mixture of the alcohols with mesylchloride in dichloromethane–triethylamine and separated by chromatography (silica gel, 80 times by weight, elution with dichloromethane–ether, 93:7).

r-1-[(Methanesulfonyloxy)methyl]-1-methyl-*c*-2-(phenylsulfonyl)cyclopropane (*cis*-**3b** mesylate, Ar = Ph): mp 95–96 °C (hexane–ethyl acetate); NMR (80) δ 1.24 (dd, 1, J^1 = 5.8, J^2 = 8.3, C_3 *t*-H), 1.30 (s, Me), 1.64 (t, 1, J = 5.9, C_3 *c*-H), 2.44 (dd, 1, J^1 = 5.9, J^2 = 8.4, C_2 H), 3.06 (s, Me), 4.66 (s, 2, CH_2OMs), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1350, 1304, 1167, 1145, 1085, 975, 950 cm^{-1}. Anal. ($C_{12}H_{16}O_5S_2$) C, H.

r-1-[(Methanesulfonyloxy)methyl]-1-methyl-*t*-2-(phenylsulfonyl)cyclopropane (*trans*-**3b** mesylate): NMR (80) δ 1.23–1.65 (m, 2, C_3 H), 1.54 (s, Me), 2.59 (dd, 1, J^1 = 5.8, J^2 = 8.9, C_2 H), 2.96 (s, Me), 3.95 (AB q, 2 J_{AB} = 10.7, $\Delta\nu \approx 17$ Hz, CH_2OMs), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1345, 1310, 1175, 1150, 1090, 955 cm^{-1}; mass spectrum, *m/e* 304 (M^+), 169, 163, 85, 83.

***cis*- and *trans*-3b (Ar = *p*-tolyl).** The two isomers were obtained and separated as above, in similar yields.

r-1-(Hydroxymethyl)-1-methyl-*c*-2-(*p*-tolylsulfonyl)cyclopropane (*cis*-**3b**, Ar = *p*-tolyl): NMR δ 1.12 (dd, 1, J^1 = 5.5, J^2 = 8.5, C_3 *t*-H), 1.26 (s, Me), 1.57 (t, 1, J = 5.5, C_3 *c*-H), 2.34 (dd, 1, J^1 = 5.5, J^2 = 8.5, C_2 H), 2.46 (s, Me), 2.60 (br, OH), 4.00 (br s, 2, CH_2OH), 7.39 and 7.86 (AB-like, 4); IR ($CHCl_3$) 3510, 1290, 1143, 1105, 1095, 1020 cm^{-1}. 3,5-Dinitrobenzoate: mp 194–195 °C (ethanol); mass spectrum, *m/e* 434 (M^+), 377, 279, 195, 149, 139, 91. Anal. ($C_{19}H_{18}N_2O_8S$) C, H, N.

r-1-(Hydroxymethyl)-1-methyl-*t*-2-(*p*-tolylsulfonyl)cyclopropane (*trans*-**3b**, Ar = *p*-tolyl): NMR δ 1.1–1.45 (m, 2, C_3 H), 1.47 (s, Me), 2.43 (s, Me), 2.46 (dd, 1 J^1 = 5.5, J^2 = 8.5, C_2 H), 3.42 (close AB q, 2, $J \approx 12$, CH_2OH), 7.35 and 7.82 (AB-like, 4); IR ($CHCl_3$) 3450, 1302, 1149, 1089, 909 cm^{-1}. 3,4-Dinitrobenzoate: mp 135–136 °C (ethanol); mass spectrum, *m/e* 434 (M^+), 377, 279, 195, 149, 139, 91. Anal. ($C_{19}H_{18}N_2O_8S$) C, H, N.

The **3b** acetates (Ar = *p*-tolyl) were prepared from a mixture of the alcohols with acetic anhydride in pyridine and separated by chromatography, the order of elution (ether–hexane, 2:3) being reversed in this case.

r-1-(Acetoxymethyl)-1-methyl-*t*-2-(*p*-tolylsulfonyl)cyclopropane (*trans*-**3b** acetate, Ar = *p*-tolyl), mp 57–58 °C (hexane); NMR δ 1.42 (m, 2), 1.47 (s, C_1 Me), 1.94 (s, CH_3CO), 2.46 (s, Me), 2.55 (dd, 1, partly hidden, C_2 H), 3.86 (s, 2, CH_2OAc), 7.38 and 7.85 (AB-like, 4); IR ($CHCl_3$) 1736, 1300, 1232, 1150, 1090, 1033 cm^{-1}. Anal. ($C_{14}H_{18}O_4S$) C, H.

r-1-(Acetoxymethyl)-1-methyl-*c*-2-(*p*-tolylsulfonyl)cyclopropane (*cis*-**3b** acetate, Ar = *p*-tolyl): NMR δ 1.15 (s, C_1 Me), 1.42 (m,

2), 2.03 (s, CH_3CO), 2.40, (dd, 1, C_2 H), 2.46 (s, Me), 4.51 (AB q, 2, J = 12, $\Delta\nu \approx 12$ Hz, CH_2OAc), 7.38 and 7.85 (AB-like, 4); IR ($CHCl_3$) 1724, 1304, 1205, 1140, 1095, 1028 cm^{-1}. Separate acetylation of the first eluted alcohol (*cis*-**3b**, Ar = *p*-tolyl) furnished the second eluted acetate (*cis*-**3b** acetate, Ar = *p*-tolyl).

The propionate ester of *trans*-**3b** (Ar = *p*-tolyl) was prepared from the alcohol with propionyl chloride in pyridine and was purified by filtration on silica gel (20 times by weight) with dichloromethane–ether (9:1): NMR δ 1.00 (t, 3, J = 7.5, CH_2CH_3), 1.2–1.6 (m, 2, C_3 H), 1.42 (s, C_1 Me), 2.22 (q, 2, J = 7.5, CH_2CH_3), 2.57 (dd, 1, C_2 H), 3.74 (close AB q, 2, $J \approx 12$, CH_2OCOEt), 7.37 and 7.83 (AB-like, 4). The reaction of this ester with BuLi to furnish **4b** is described further below.

trans-1-(1-Hydroxy-2-methylpropyl)-2-(phenylsulfonyl)cyclopropane (**3c**, Ar = Ph): mp 52–53 °C (pentane–ether); yield 88%; NMR δ 0.91 (2 d, 6, J = 7, 2 Me), 1.0–2.1 (m, 4), 2.0 (s, OH), 2.50 (dt, 1, J^1 = 8, $J^2 = J^3$ = 5, C_2 H), 3.22 (t, 1, J = 5, CHOH), 7.5–8.0 (m, 5); IR (KBr) 1290, 1143 cm^{-1}. Anal. ($C_{13}H_{18}O_3S$) C, H. *p*-Toluenesulfonate ester (**3c** tosylate, Ar = Ph), mp 110–111 °C (ether–hexane). Anal. ($C_{20}H_{24}O_5S_2$) C, H.

trans-1-(1-Hydroxy-2-methylpropyl)-2-(*p*-tolylsulfonyl)cyclopropane (**3c**, Ar = *p*-tolyl): mp 58–59 °C (pentane–ether); yield 88%; NMR δ 0.97 (d, 6, J = 7, 2 Me), 1.0–2.0 (m, 4), 2.45 (s and m, 5, Me, C_2 H and OH), 3.19 (t, 1, CHOH), 7.37 and 7.80 (AB-like, 4); IR (KBr) 3330, 1302, 1150 cm^{-1}. Anal. ($C_{14}H_{20}O_3S$) C, H.

trans-1-(1-Hydroxy-1-methylethyl)-2-(phenylsulfonyl)cyclopropane (**3d**, Ar = Ph): mp 70–71 °C (hexane–benzene); yield 77%; NMR δ 1.05 (s, Me), 1.21 (s, Me), 1.2–2.0 (m, 3), 2.56 (m, 1), 7.5–8.0 (m, 5); IR ($CHCl_3$) 3450, 1300, 1143 cm^{-1}. Anal. ($C_{12}H_{16}O_3S$) C, H.

trans-1-(1-Hydroxy-1-methylethyl)-2-(*p*-tolylsulfonyl)cyclopropane (**3d**, Ar = *p*-tolyl): yield 92%; NMR δ 1.10 (s, Me), 1.23 (s, Me), 1.2–1.9 (m, 3), 2.00 (s, OH), 2.45 (s, Me), 2.58 (m, 1), 7.37 and 7.82 (AB-like, 4); IR ($CHCl_3$) 3450, 1300, 1136 cm^{-1}; mass spectrum, m/e 254 (M^+), 239, 183, 139, 91.

trans-1-(1-Hydroxycyclopentyl)-2-(phenylsulfonyl)cyclopropane (**3e**): mp 64–66 °C (benzene–hexane); yield 87%; NMR δ 1.0–2.0 (m, 11), 2.4 (s, OH), 2.59 (dt, 1, J^1 = 8.5, $J^2 = J^3$ = 5.5, C_2 H), 7.5–8.1 (m, 5); IR (KBr) 3400, 1295, 1150 cm^{-1}; mass spectrum, m/e 266 (M^+), 237, 224, 169, 143, 125, 107, 97, 91. Anal. ($C_{14}H_{18}O_3S$) C, H.

trans-1-(1-Hydroxycyclohexyl)-2-(phenylsulfonyl)cyclopropane (**3f**): mp 99–100 °C (benzene–hexane); yield 92%; NMR δ 1.1–2.1 (m, 14), 2.60 (dt, 1, J^1 = 8, $J^2 = J^3$ = 5, C_2 H), 7.5–8.1 (m, 5); IR (KBr) 3450, 1300, 1150, 1092 cm^{-1}. Anal. ($C_{15}H_{20}O_3S$) C, H.

***cis*- and *trans*-3g.** The crude reaction product was chromatographed on silica gel (80 times by weight; elution with ether–hexane, 3:2) to furnish 79% total yield of the two alcohols in a ratio of ca. 1:3 by order of elution, and 12% of recovered epoxide **2g**.

(1*RS*,3*SR*,4*RS*)-4-Hydroxy-1-(phenylsulfonyl)spiro[2.5]octane (*trans*-**3g**); NMR (80) δ 1.2–2.3 (m, 9), 1.34 (d, 2, J = 7, C_2 H), 2.72 (t, 1, J = 7, C_1 H), 3.55 (br, 1, CHOH), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1306, 1145, 1088 cm^{-1}.

(1*SR*,3*SR*,4*RS*)-4-Hydroxy-1-(phenylsulfonyl)spiro[2.5]octane (*cis*-**3g**): mp 116–117 °C (benzene–hexane); NMR (80) δ 0.9–2.3 (m, 12) with two visible double doublets on top, 1.07 (dd, 1, J^1 = 5.3, J^2 = 8.3), 2.22 (dd, 1, J^1 = 6.0, J^2 = 8.3), 4.39 (br s, 1, CHOH), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1320, 1307, 1147, 1105, 1070 cm^{-1}. Anal. ($C_{14}H_{18}O_3S$) C, H.

2-*exo*-Hydroxy-7-*exo*-(phenylsulfonyl)bicyclo[4.1.0]heptane (**3h**): 89% yield from *trans*-**2h**; NMR (80) δ 0.75–2.2 (m, 10), 3.92 (br, 1, CHOH), 7.5–8.0 (m, 5); IR ($CHCl_3$) 3450 br, 1307, 1147, 1088 cm^{-1}. *p*-Toluenesulfonate ester, mp 100–101 °C (ethyl acetate–hexane). Anal. ($C_{20}H_{22}O_5S_2$) C, H.

Bicyclic Sulfones 4. The esters *trans*-**3b** acetate and *trans*-**3b** propionate (Ar = *p*-tolyl) were treated in THF with BuLi as described above for the preparation of compounds **3**. The acetate ester provided in 50% yield 2-hydroxy-2,5-dimethyl-1-(*p*-tolylsulfonyl)-3-oxabicyclo[3.1.0]hexane (**4a**): mp 124–125 °C (hexane); NMR δ 0.93 (s, C_2 Me), 1.18 and 1.86 (AB q, 2, J = 5.0, C_6 H), 1.67 (s, C_5 Me), 2.46 (s, Me), 3.82 (AB q, 2 J = 8.5, $\Delta\nu \approx 14$ Hz, C_4 H), 4.25 (br, OH), 7.37 and 7.87 (AB-like, 4); IR (KBr) 3350, 1295, 1176, 1150, 1120, 1100, 1075, 1026, 952 cm^{-1}. Anal. ($C_{14}H_{18}O_4S$) C, H.

The propionate ester provided a bicyclic sulfone in 85% yield by direct crystallization of the crude product from hexane–ether and recrystallization from ethanol. 2-Ethyl-2-hydroxy-5-methyl-1-(*p*-tolylsulfonyl)-3-oxabicyclo[3.1.0]hexane (**4b**): mp 155–156 °C; NMR δ 0.75 (t, J = 6.5, CH_2CH_3), 1.05–1.45 (m, 3, CH_2CH_3 and C_6 H), 1.67 (s, C_5 Me), 1.85 (d, 1, J = 5.0, C_6 H), 2.46 (s, Me), 3.83 (AB q, 2, J = 9, $\Delta\nu \approx 14$ Hz, C_4 H), 7.38 and 7.88 (AB-like, 4); IR (KBr) 3420, 1300, 1167, 1152, 1132, 1108, 1078, 1032, 932 cm^{-1}. Anal. ($C_{15}H_{20}O_4S$) C, H.

Dehydration of Alcohol 3: Vinylcyclopropanes 5. Dehydrations were carried out by refluxing alcohol **3** in benzene (5–10 mL/mmol) in the presence of *p*-toluenesulfonic acid (0.1–0.2 molar equiv) and with azeotropic removal of water. The cooled benzene solution was washed with aqueous sodium carbonate solution and with water and dried. Purification of the crude product and occasional separation from unreacted starting material was achieved by simple chromatography (10–20 times of silica gel by weight) followed by crystallization. The yields indicated are of recrystallized products relative to total starting material.

trans-1-(1-Methylvinyl)-2-(phenylsulfonyl)cyclopropane (**5a**, Ar = Ph): mp 51–52 °C (hexane); yield 80%; NMR δ 1.1–1.8 (m, 2), 1.55 (t, $J \approx 1$, Me), 2.1–2.55 (m, 2), 4.57 (q, $J \approx 1$, methene), 7.5–8.0 (m, 5); IR (KBr) 1282, 1142, 917, 904 cm^{-1}; mass spectrum, m/e 222 (M^+), 143, 129, 125, 97. Anal. ($C_{12}H_{14}O_2S$) C, H.

trans-1-(1-Methylvinyl)-2-(*p*-tolylsulfonyl)cyclopropane (**5a**, Ar = *p*-tolyl): mp 62–63 °C (hexane); yield 72%; NMR δ 1.05–1.75 (m, 2), 1.58 (t, $J \approx 1$, Me), 2.15–2.65 (m, 2), 2.46 (s, Me), 4.78 (q, $J \approx 1$, methene), 7.38 and 7.84 (AB-like, 4); IR (KBr) 1290, 1150, 1087, 1061, 952, 905 cm^{-1}; mass spectrum, m/e 236 (M^+), 172, 157, 142, 139, 91. Anal. ($C_{13}H_{16}O_2S$) C, H.

trans-1-(2-Methyl-1-propen-1-yl)-2-(phenylsulfonyl)cyclopropane (**5b**, Ar = Ph): mp 80–81 °C (hexane); up to 86% yield; NMR δ 0.85–1.2 (m, 1), 1.5–1.85 (m, 1), 1.67 (br s, 2 Me), 2.25–2.55 (m, 2), 4.65 (br d, 1), 7.5–8.1 (m, 5); IR (KBr) 1295, 1144 cm^{-1}; mass spectrum, m/e 236 (M^+), 163, 157, 143, 125, 115, 100, 96, 95, 93, 91. Anal. ($C_{13}H_{16}O_2S$) C, H.

trans-1-(2-Methyl-1-propen-1-yl)-2-(*p*-tolylsulfonyl)cyclopropane (**5b**, Ar = *p*-tolyl): mp 93–94 °C (hexane); yield 73%; NMR δ 0.8–1.2 (m, 1), 1.68 (br s and m, 7, 2 Me and 1 H), 2.35 (m, 2), 2.45 (s, Me), 4.65 (br d, 1), 7.40 and 7.85 (AB-like, 4); IR (KBr) 1295, 1145 cm^{-1}. Anal. ($C_{14}H_{18}O_2S$) C, H.

trans-1-(Cyclopenten-1-yl)-2-(phenylsulfonyl)cyclopropane (**5c**), mp 83–84 °C (hexane); yield 65%; NMR δ 1.0–2.6 (m, 10), 5.5 (br s, 1), 7.5–8.1 (m, 5); IR (KBr) 1305, 1144, 1087 cm^{-1}; mass spectrum, m/e 248 (M^+), 125, 107, 91. Anal. ($C_{14}H_{16}O_2S$) C, H.

trans-1-(Cyclohexen-1-yl)-2-(phenylsulfonyl)cyclopropane (**5d**): mp 46–47 °C (ethanol); yield 70%; NMR δ 1.0–2.6 (m, 12), 5.50 (br t, 1), 7.5–8.1 (m, 5); IR (KBr) 1307, 1145, 1087 cm^{-1}. Anal. ($C_{15}H_{18}O_2S$) C, H.

Preparation of Epoxides 6. Epoxidation of sulfones **5** was carried out as for **2** above, except for **5c** (see below). The mixture of two diastereomeric epoxides thus obtained was purified by chromatography, with occasional partial separation or enrichment in one or the other isomers.

trans-1-(1,2-Epoxy-1-methylethyl)-2-(phenylsulfonyl)cyclopropane (**6a**, Ar = Ph): yield 64%; NMR δ 0.75–1.65 (m, 2), 1.18 and 1.35 (2 s, 3, two diastereomeric Me), 1.9–2.7 (m, 4), 7.5–8.1 (m, 5); IR ($CHCl_3$) 1300, 1145 cm^{-1}.

trans-1-(1,2-Epoxy-2-methylpropyl)-2-(phenylsulfonyl)cyclopropane (**6b**, Ar = Ph), yield 82–86%. Careful chromatography (100 times silica gel by weight; elution with hexane–ether, 7:3) separated small amounts of the pure isomers in the first and last fractions. Isomer I: mp 111–112 °C (hexane); NMR δ 1.26 (s, 6, 2 Me), 0.95–2.13 (m, 3, C_1 H and C_3 H), 2.5–2.8 (d and m, 2, C_2 H and epoxidic H), 7.5–8.1 (m, 5) [when C_2 H was replaced by deuterium, a one-proton doublet was observed at δ 2.53 (epoxidic H) and the upper field multiplet appeared simplified]; IR (KBr) 1295, 1144 cm^{-1}; mass spectrum (of deuterated compound), m/e 253 (M^+), 210, 170, 143, 125, 112, 96, 94. Anal. ($C_{12}H_{16}O_3S$) C, H. Isomer II did not solidify: NMR δ 1.22 (s, 6, 2 Me), 1.05–2.1 (m, 3), 2.4–2.7 (m, 2), 7.5–8.1 (m, 5), differing from isomer I in the fingerprint of the multiplets; IR ($CHCl_3$) 1300, 1145 cm^{-1}.

trans-1-(1,2-Epoxy-2-methylpropyl)-2-(*p*-tolylsulfonyl)cyclopropane (**6b**, Ar = *p*-tolyl): mp 90–93 °C (diastereomeric mixture); yield 88%; NMR δ 1.28 (s, 6, 2 Me), 0.9–2.1 (m, 3), 2.46 (s, M),

2.4–2.8 (m, 3), 7.47 and 7.83 (AB-like, 4). One pure diastereomer was recovered from reaction of **6b** with BuLi (see below): mp 96–97 °C (hexane); same NMR as above, with simplified multiplets. Anal. ($C_{14}H_{18}O_3S$) C, H.

trans-1-(1,2-Epoxycyclopentyl)-2-(phenylsulfonyl)cyclopropane (**6c**): mp 64–65 °C (diastereomeric mixture, 1:1); 95% yield by epoxidation under the above conditions with added 5% aqueous sodium bicarbonate (100 mL/0.05 mmol of sulfone) and vigorous stirring; NMR (80) δ 0.9–2.6 (m, 10), 3.05 and 3.20 (2 s, 1, two diastereomeric epoxidic protons), 7.5–8.0 (m, 5). A small amount of one pure isomer (isomer I) fortuitously precipitated from a chloroform–ether solution. This was then used to achieve separation of the isomers as follows. The mixture of isomers from epoxidation of 2.3 g of **5c** was dissolved in ethanol (7 mL), seeded with isomer I, and cooled overnight at 0 °C. The precipitate (1.026 g) was collected and recrystallized from ethanol, yielding 0.86 g of pure isomer I. The residue from the first filtration was passed on silica gel (30 g) with hexane–ethyl acetate (1:1), yielding 1.12 g of ca. 9:2 mixture of isomers II and I, respectively. Isomer I: mp 104–105 °C; NMR (80), same as above but with only one sharp one-proton singlet at δ 3.20; IR ($CHCl_3$) 1310, 1150, 1090 cm^{-1}. Anal. ($C_{14}H_{16}O_3S$) C, H.

Isomerization of 6c to Ketone 8. Epoxides **6c** (0.28 g) were refluxed in benzene–dichloromethane (1:1; 30 mL) for 0.5 h in the presence of *p*-toluene sulfonic acid (0.02 g). The crude product was chromatographed on silica gel (15 g; elution with hexane-ethyl acetate, 2:1) to yield starting epoxide (10 mg) and *trans*-2-(2-oxocyclopentyl)-1-(phenylsulfonyl)cyclopropane (**8**): 0.19 g (68%); NMR (80) δ 1.0–2.6 (m, 11), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1740, 1307, 1145, 1087 cm^{-1}; mass spectrum, *m/e* 264 (M^+), 209, 123, 95. 2,4-Dinitrophenylhydrazone, mp 188–189 °C (ethyl acetate). Anal. ($C_{20}H_{20}N_4O_6S$) C, H, N.

Ketone **8** was also obtained by chromatography of samples of epoxides **6c** which had been kept at room temperature for a few weeks.

Preparation of Bicyclobutanes 7 and Diiodides 10. A solution of epoxides **6** in THF was treated with BuLi (2 molar equiv) at −70 °C. The cold bath was removed, and the reaction mixture was stirred and allowed to warm to room temperature for 2–3 h. The crude product mixture was separated and purified by chromatography.

Iodine addition products (**10**) of most of the bicyclobutanes (**7** and **9**) were prepared by adding a chloroform solution of the element to the bicyclic sulfone in chloroform until the color persisted. The solvent was then evaporated, occasionally after washing with aqueous sodium thiosulfate, and the product was usually purified by filtration on silica gel and crystallization.

A diastereomeric mixture of epoxides **6a** (Ar = Ph) furnished two isomeric compounds **7a** in 12% yield each.

2-*exo*-(Hydroxymethyl)-2-*endo*-methyl-1-(phenylsulfonyl)bicyclo[1.1.0]butane (*cis*-**7a**, Ar = Ph): NMR δ 0.91 (s, Me), 1.80 (t, 1, J = 2, C_4 *endo*-H), 2.30 (s, OH), 2.37 (dd, 1, J^1 = 4, J^2 = 2, C_4 *exo*-H), 3.07 (dd, 1, J^1 = 4, J^2 = 2, C_3 H), 3.92 (br, 2, CH_2OH), 7.5–8.1 (m, 5). 3,5-Dinitrobenzoate: mp 163–164 °C (ether); NMR δ 1.11 (s, Me), 1.94 (t, 1, J = 2.2, C_4 *endo*-H), 2.57 (dd, 1, J^1 = 4, J^2 = 2.2, C_4 *exo*-H), 3.09 (dd, 1, J^1 = 4, J^2 = 2.2, C_3 H), 4.83 (AB q, J = 12 $\Delta\nu \approx$ 14 Hz, CH_2OR), 7.5–8.1 (m, 5), 9.70 (m, 3); mass spectrum, *m/e* 432 (M^+), 415, 291, 263, 237, 220, 195, 179, 165, 149, 143, 125, 103, 95. Anal. ($C_{19}H_{16}N_2O_8S$) C, H, N.

2-*endo*-(Hydroxymethyl)-2-*exo*-methyl-1-(phenylsulfonyl)bicyclo[1.1.0]butane (*trans*-**7a**, Ar = Ph): NMR δ 1.63 (s, Me), 1.70 (br, OH), 1.92 (t, 1, J = 2, C_4 *endo*-H), 2.57 (dd, 1, J^1 = 4, J^2 = 2.5, C_4 *exo*-H), 2.77 (dd, 1 J^1 = 4, J^2 = 2.5, C_3 H), 3.37 (s, 2, CH_2OH), 7.5–8.1 (m, 5). 3,5-Dinitrobenzoate: mp 153–154 °C (ether); NMR δ 1.73 (s, Me), 2.14 (t, 1, J = 2.5, C_4 *endo*-H), 2.74 (dd, 1, J^1 = 4, J^2 = 2.5, C_4 exo-H), 2.94 (dd, 1, J^1 = 4, J^2 = 2.5, C_3 H), 4.30 (AB q, 2, J = 12, $\Delta\nu \approx$ 14 Hz, CH_2OR), 7.3–8.0 (m, 5), 9.47 (d, 2), 9.77 (t, 1); mass spectrum, *m/e* 432 (M^+), 291, 290, 237, 227, 195, 179, 149, 125, 103, 95. Anal. ($C_{19}H_{16}N_2O_8S$) C, H, N.

When submitted to the above reaction, solid **6b** (Ar = Ph; isomer I) was recovered practically unchanged. A 66% yield of one **7b** isomer was, however, obtained from **6b** (Ar = Ph) chromatographically enriched in isomer II.

2-*exo*-(1-Hydroxy-1-methylethyl)-1-(phenylsulfonyl)bicyclo[1.1.0]butane (*cis*-**7b**, Ar = Ph): mp 57–58 °C (hexane); NMR (80) δ 1.08 (d, 1, J = 2, C_4 *endo*-H), 1.32 (s, Me), 1.46 (s, Me), 1.68 (d, 1, J = 2, C_2 *endo*-H), 2.16 (d, 1, J = 3.1, C_2 *exo*-H), 3.18 (pentuplet, 1, J^1 = 4, J^2 = J^3 = 2, C_3 H), 4.05 (s, OH), 7.5–8.1 (m, 5) [for 3-D-*cis*-7b: δ 1.08 (s, 1), 1.32 (s, Me), 1.46 (s, Me), 1.68 (s, 1), 2.17 (s, 1), 4.1 (br, OH), 7.5–8.1 (m, 5)]; IR (KBr) 1295, 1183, 1140, 1083, 944, 876, 839, 814 cm^{-1}; mass spectrum, *m/e* 252 (M^+), 237, 209, 194, 143, 125, 111, 110, 109, 95. Anal. ($C_{13}H_{16}O_3S$) C, H.

Iodine adduct 2-(1-hydroxy-1-methylethyl)-1,3-diiodo-1-(phenylsulfonyl)cyclobutane (**10a**, Ar = Ph): mp 158–159 °C (benzene–hexane); NMR δ 1.37 (s, Me), 1.41 (s, Me), 2.08 (br s, OH), 2.7–3.8 (m, 3), 4.72 (q, 1, J = 9), 7.5–8.1 (m, 5); mass spectrum, *m/e* 506 (M^+), 337, 321, 179, 143, 125. Anal. ($C_{13}H_{16}I_2O_3S_2$) C, H.

Similar results were obtained from **6b** (Ar = *p*-tolyl).

2-*exo*-(1-Hydroxy-1-methylethyl)-1-(*p*-tolylsulfonyl)bicyclo[1.1.0]butane (*cis*-**7b**, Ar = *p*-tolyl): mp 97–98 °C (hexane); up to 70% yield from mixtures rich in the more reactive liquid epoxide; NMR δ 1.05 (d, 1, $J \approx$ 2, C_4 *endo*-H), 1.32 (s, Me), 1.44 (s, Me), 1.65 (d, 1, J = 2, C_2 *endo*-H), 2.13 (d, 1, J = 4, C_4 *exo*-H), 2.46 (s, Me), 3.15 (pentuplet, 1, J^1 = 4, J^2 = J^3 = 2, C_3 H), 4.10 (s, OH), 7.43 and 7.88 (AB-like, 4). Anal. ($C_{14}H_{18}O_3S$) C, H.

Iodine adduct 2-(1-hydroxy-1-methylethyl)-1,3-diiodo-1-(*p*-tolylsulfonyl)cyclobutane (**10a**, Ar = *p*-tolyl), mp 116–117 °C (hexane). Anal. ($C_{14}H_{18}I_2O_3S$) C, H.

A minute amount of a second, slightly impure **7b** isomer was obtained here from chromatographic separation, 2-*endo*-(1-hydroxy-1-methylethyl)-1-(*p*-tolylsulfonyl)bicyclo[1.1.0]butane (*trans*-**7b**, Ar = *p*-tolyl): mp 93–95 °C (hexane); NMR δ 1.12 (s, Me), 1.21 (s, Me), 2.51, 2.71, 2.87, 3.32 (all m, 4, ring protons), 7.31 and 7.80 (AB-like, 4).

Four **7c** isomers (membered I–IV by order of elution) were obtained from a diastereomeric mixture **6c** in yields totaling up to 70% and with a slight preponderance of isomers II and IV. Separation was achieved by chromatography using 80 times, by weight, of silica gel and eluting with ether–hexane mixtures (1:1 to 3:1). Alternatively, reactions were carried out on one pure **6c** isomer (mp 104–105 °C) or on a mixture enriched in the second isomer. Isomers II and III of **7c** were obtained from the solid **6c** isomer and mainly isomers I and IV from the second isomer. Quenching of the reaction with deuterium oxide provided deuterated compounds with the ^1H NMR spectral properties described below.

(1*RS*,2*RS*)-2-Hydroxycyclopentane-1-spiro-2′-[(1′*RS*,3′*SR*)-1′-(phenylsulfonyl)bicyclo[1.1.0]butane] (**7c**-I); NMR (80) δ 1.25–1.86 (m, 7), 2.26 (dd, 1, $J_{cis\text{-}3',4'}$ = 3.9, J_{gem} = 1.9, $C_{4'}$ *exo*-H), 2.74 (dd, 1, $J_{cis\text{-}3',4'}$ = 3.8, $J_{trans\text{-}3',4'}$ = 2.7, $C_{3'}$ H), 3.80 (s or d, 1, OH), 4.12 (br s, 1, CHOH), 7.5–8.0 (m, 5); NMR (80) of 3′-D-7c-I δ 1.25–1.86 (m, with a distinguishable d at 1.67 (1, J_{gem} = 1.9, $C_{4'}$ *endo*-H), 2.34 (d, 1, J_{gem} = 1.9, $C_{4'}$ *exo*-H), no signal at 2.74, and other signals unchanged; IR ($CHCl_3$) 3500, 1305, 1155 cm^{-1}.

Iodine adduct 8-hydroxy-1,3-diiodo-1-(phenylsulfonyl)spiro[3.4]octane (**10b**-I): mp 177–178 °C (hexane); NMR (80) δ 1.25–2.9 (m, 7), 2.77 (dd, 1, J_{AB} = 12.7, J_{BX} = 7.5, C_2 H), 3.61 (dd, 1, J_{AB} = 12.7, J_{AX} = 10.3, C_2 H), 4.10 (br s, 1, CHOH), 4.53 (dd, 1, J_{XA} = 10.3, J_{XB} = 7.5, C_3 H), 7.3–8.0 (m, 5); mass spectrum, *m/e* 391 (M^+ − 127). Anal. ($C_{14}H_{16}I_2O_3S$) C, H.

(1*RS*,2*SR*)-2-Hydroxycyclopentane-1-spiro-2′-[(1′*RS*,3′*SR*)-1′-(phenylsulfonyl)bicyclo[1.1.0]butane] (**7c**-II): NMR (80) δ 1.5–1.7 (m, 7), 1.66 (dd, 1, $J_{trans\text{-}3',4'}$ = 2.7, J_{gem} = 1.7, $C_{4'}$ *endo*-H), 3.16 (dd, 1, J_{cis} = 4.0, J_{trans} = 2.7, $C_{3'}$ H), 3.52 (d, 1, OH; exchanged with D_2O), 7.5–8.0 (m, 5); NMR (80) of 3′-D-**7c**-II δ 1.66 (d, 1, J = 1.7), 2.44 (d, 1, J = 1.7); no signal at 3.16, other signals unchanged; IR ($CHCl_3$) 3500, 1308, 1292, 1150, 1125, 1089, 1072 cm^{-1}.

Iodine adduct 8-hydroxy-1,3-diiodo-1-(phenylsulfonyl)spiro[3.4]octane (**10b**-II): mp 117–118 °C (pentane); NMR (80) δ 1.5–2.74 (m, 6), 2.68 (dd, 1, J_{AB} = 14.8, J_{BX} = 5.3, C_2 H), 3.74 (dd, 1, J_{AB} = 14.8, J_{AX} = 8.9, C_2 H), 3.90 (d, 1, OH), 5.03 (dt, 1; t with added D_2O, J = 7, CHOH), 5.26 (dd, 1, J_{XA} = 8.9, J_{XB} = 5.3, C_3 H), 7.5–8.0 (m, 5); mass spectrum, *m/e* 391 (M^+ − 127). Anal. ($C_{14}H_{16}I_2O_3S$) C, H.

(1*SR*,2*SR*)-2-Hydroxycyclopentane-1-spiro-2′-[(1′*RS*,3′*SR*)-1′-(phenylsulfonyl)bicyclo[1.1.0]butane] (**7c**-III): NMR (80) δ 1.05–2.5 (m, 8), 2.65 (m, 2, narrow AB part of an ABX spectrum, $\Delta\nu \approx$ 7 Hz, $C_{4'}$ *exo*-H and $C_{3'}$ H), 3.69 (br s, 1, CHOH), 7.5–8.0 (m, 5); NMR (80) of 3′-D-**7c**-III δ 1.82 (d, J = 2.1, $C_{4'}$ *endo*-H),

2.62 (d, 1, J = 2.1, $C_{4'}$ *exo*-H), no signal to the lower field side of this doublet, other signals unchanged; IR ($CHCl_3$) 1312, 1295, 1150, 1125, 1088 cm^{-1}.

Iodine adduct 5-hydroxy-1,3-diiodo-1-(phenylsulfonyl)spiro-[3.4]octane (**10b**-III): mp 143–144 °C (pentane); NMR (80) δ 1.25–2.4 (m, 6), 3.01 (dd, 1, J_{AB} = 14.8, J_{BX} = 8.7, C_2 H), 3.60 (dd, 1, J_{AB} = 14.8, J_{AX} = 7.6, C_2 H), 3.98 (d, 1, OH), 4.40 (dd, 1, J_{XA} = 7.6, J_{XB} = 8.7, C_3 H), 4.74 (br t, 1, CHOH), 7.5–8.1 (m, 5); mass spectrum, m/e 391 (M^+ –127). Anal. ($C_{14}H_{16}I_2O_3S$) C, H.

(1*SR*,2*RS*)-2-Hydroxycyclopentane-1-spiro-2′-[(1′*RS*,3′*SR*)-1′-(phenylsulfonyl)bicyclo[1.1.0]butane] (**7c**-IV): NMR (80) δ 1.3–2.5 (m, 8), 2.65 (AB part of an ABX spectrum, 2, J_{AB} = 4.0, J_{AX} = 2.7, J_{BX} = 1.8, $C_{4'}$ *exo*-H and $C_{3'}$ H), 3.75 (br s, 1, CHOH), 7.5–8.0 (m, 5); NMR (80) of 3′-D-**7c**-IV δ 1.81 (d, J = 1.8, $C_{4'}$ *endo*-H), 2.58 (d, 1, J = 1.8, $C_{4'}$ *exo*-H), no signal to lower-field side of this doublet, other signals unchanged; IR ($CHCl_3$) 3450, 1305, 1148 cm^{-1}.

Iodine adduct 5-hydroxy-1,3-diiodo-1-(phenylsulfonyl)spiro-[3.4]octane (**10b**-IV): mp 171–172 °C (hexane); NMR (80) δ 1.2–2.7 (m, 7), 2.65 (dd, 1, J_{AB} = 12.2, J_{BX} = 7.5, C_2 H), 3.60 (dd, 1 J_{AB} = 12.2, J_{AX} = 11.0, C_2 H), 4.63 (dd, 1, J_{XA} = 11.0, J_{XB} = 7.5, C_3 H), 5.20 (t, 1, J = 7.3, CHOH), 7.5–8.0 (m, 5); mass spectrum, m/e 391 (M^+ – 127). Anal. ($C_{14}H_{16}I_2O_3S$) C, H.

Preparation of Bicyclobutanes 9. To a stirred solution of epoxide **2** in THF (5–7 mL/mmol; 1–20 mmol of **2**) cooled with ice and ice–water were added 1 molar equivalent each of BuLi, methanesulfonyl chloride (2 N in THF), and BuLi. The total addition and reaction time for each individual step was 3–5 min, as determined by TLC monitoring. In some cases, especially for **2a**, quenching with water or ammonium chloride solution was done almost immediately after addition of the second equivalent of BuLi in order to avoid a fast drop in the yield. The usual workup and chromatography on silica gel (10–30 times by weight of crude product; elution with ether–hexane mixtures) provided **9**, mostly as solid stable compounds.

Bicyclobutanes **9** were also similarly obtained from the intermediate alcohols **3** or their methanesulfonate or *p*-toluenesulfonate esters by applying the last two or one steps, respectively.

1-(Phenylsulfonyl)bicyclo[1.1.0]butane (**9a**): mp 81–82 °C (hexane); 45–54% yield from **2a** or 55–60% from **3a** mesylate; NMR (80) δ 1.39 (s, $W_{1/2}$ = 4 Hz, fine splitting at the top, 2, C_2 and C_4 *endo*-H), 2.56 (s, $W_{1/2}$ = 2 Hz, on top of a narrow m, 3, C_2 and C_4 *exo*-H and C_3 H), 7.5–8.0 (m, 5); IR (KBr) 1305, 1145, 1112, 1013, 818, 765, 752 cm^{-1}; mass spectrum, m/e 194 (M^+), 142, 129, 128, 127, 126, 125, 115, 97, 94, 91. Anal. ($C_{10}H_{10}O_2S$) C, H.

Iodine adduct 1,3-diiodo-1-(phenylsulfonyl)cyclobutane (**10c**): mp 149–150 °C (ether); NMR (80) δ 2.8–4.1 (m, 4), 4.54–4.92 (m, 1), 7.5–8.1 (m, 5); mass spectrum, m/e 448 (M^+), 321 (M^+ – I), 180, 125. Anal. ($C_{10}H_{10}I_2O_2S$) C, H.

3-Methyl-1-(phenylsulfonyl)bicyclo[1.1.0]butane (**9b**): mp 60–61 °C (pentane); obtained from *cis*- and *trans*-**3b** mesylates (Ar Ph) in ca. 80% yield; NMR (80) δ 1.31 (s, 2, C_2 and C_4 *endo*-H), 1.88 (s, Me), 2.33 (s, 2, C_2 and C_4 *exo*-H), 7.5–8.0 (m, 5); IR (KBr) 1305, 1290, 1142, 1105, 1072, 937, 797, 725 cm^{-1}; mass spectrum, m/e 208 (M^+), 143, 129, 126, 125, 83. Anal. ($C_{11}H_{12}O_2S$) C, H.

Iodine adduct 1,3-diiodo-3-methyl-1-(phenylsulfonyl)cyclobutane (**10d**): mp 136–137 °C (ethanol); NMR (80) δ 2.15 (s, Me), 3.20 (AB-like, 4, $J \approx 14.5$, $\Delta\nu \approx 35$ Hz), 7.5–8.0 (m, 5); mass spectrum, m/e 462 (M^+), 335, 194, 143, 125. Anal. ($C_{11}H_{12}I_2O_2S$) C, H.

2-*exo*-(1-Methylethyl)-1-(*p*-tolylsulfonyl)bicyclo[1.1.0]butane (**9c**, *p*-tolyl instead of Ph): mp 66–67 °C (pentane); obtained in 67% yield from **2c** (Ar = *p*-tolyl); NMR (80) δ 1.01 (d and m, 7, J = 6.6, 2 Me and C_4 *endo*-H), 1.37 (dd, 1, J^1 = 9.8, J^2 = 2.3, C_2 *endo*-H), 1.7–2.3 [m, 1, $CH(CH_3)_2$], 2.30 (dd, 1, J^1 = 3.7, J^2 = 1.2, C_4 *exo*-H), 2.44 (s, Me), 2.64 (m, 1, C_3 H), 7.33 and 7.83 (AB-like, 4); IR (KBr) 1300, 1140, 1080, 945, 890, 810, 750 cm^{-1}; mass spectrum, m/e 250 (M^+), 157, 139, 111, 93, 91. Anal. ($C_{14}H_{18}O_2S$) C, H.

2-*exo*-(1-Methylethyl)-1-(phenylsulfonyl)bicyclo[1.1.0]butane (**9c**): bp 175–180 °C (bath temperature; 0.13 kPa); obtained in 91% yield from **3c** tosylate (Ar = Ph); NMR (80) δ 1.01 (d and m, 7, J = 6.6, 2 Me and C_4 *endo*-H), 1.37 (dd, J^1 = 9.8, J^2 = 2.3, C_2 *endo*-H), 1.7–2.3 [m, 1, $CH(CH_3)_2$], 2.30 (dd, 1, J^1 = 3.7, J^2 = 1.2, C_4 *exo*-H), 2.64 (m, 1, C_3 H), 7.5–8.0 (m, 5); IR 1310, 1160, 1140, 1082, 945, 880, 812 cm^{-1}. Anal. ($C_{13}H_{16}O_2S$) C, H.

Iodine adduct 1,3-diiodo-2-(1-methylethyl)-1-(phenylsulfonyl)cyclobutane (**10e**): mp 117–118 °C (ethanol); NMR (80) δ 0.89 (d, J = 6.3, Me), 1.16 (d, J = 6.4, Me), 1.8 [m, 1, $CH(CH_3)_2$], 2.34–2.88 (m, 2, C_2 and C_4 H), 3.47 (dd, 1, C_4 H), 4.12 (q, 1, C_3 H), 7.5–8.1 (m, 5); mass spectrum, m/e 490 (M^+), 363, 221, 125, 95, 94. Anal. ($C_{13}H_{16}I_2O_2S$) C, H.

2,2-Dimethyl-1-(phenylsulfonyl)bicyclo[1.1.0]butane (**9d**), bp 175–180 °C (bath temperature; 0.13 kPa); 47–51% yield from **2d** (Ar = Ph); NMR (80) δ 0.94 (s, Me), 1.53 (s, Me), 1.80 (t, 1, J = 2.2, C_4 *endo*-H), 2.46 (dd, 1, J^1 = 4.08, J^2 = 2.2, C_1 *exo*-H), 2.63 (dd, 1, J^1 = 4.0, J^2 = 2.3, C_3 H), 7.5–8.0 (m, 5); IR ($CHCl_3$) 1305, 1145, 1088, 900 cm^{-1}; mass spectrum, m/e 222 (M^+), 186, 143, 142, 126, 125, 97, 81. Anal. ($C_{12}H_{14}O_2S$) C, H.

Iodine adduct 1,3-diiodo-2,2-dimethyl-1-(phenylsulfonyl)-cyclobutane (**10f**): mp 150–151 °C (ethanol); NMR (80) δ 1.40 (s, Me), 1.85 (s, Me), 2.81 (dd, 1, J_{gem} = 12.7, $J_{3,4\text{-}trans}$ = 4.7 C_4 H), 3.68 (dd, 1, J_{gem} = 12.7, $J_{3,4\text{-}cis}$ = 10.4, C_4 H), 4.55 (dd, 1, J_{cis} = 10.4, J_{trans} = 7.4, C_3 H), 7.5–8.0 (m, 5); mass spectrum, m/e 476 (M^+), 349, 335, 295, 208, 207, 182, 128, 127, 125. Anal. ($C_{12}H_{14}I_2O_2S$) C, H.

1-(Phenylsulfonyl)tricyclo[4.1.0.0^{2,7}]heptane (**9e**): mp 52–53 °C (hexane); 54% yield from *trans*-**2h**; NMR (80) δ 1.23–1.57 (m, 6), 2.68 (t, 1, J = 3.5, C_7 H), 3.28 (br s, 2, C_2 H and C_6 H), 7.5–8.0 (m, 5); IR (KBr) 1300, 1190, 1140, 1090, 1065, 1040, 995, 858, 800 cm^{-1}; mass spectrum, m/e 234 (M^+), 143, 126, 125, 109, 92, 91. Anal. ($C_{13}H_{14}O_2S$) C, H.

7-(Phenylsulfonyl)tricyclo[5.1.0.0^{1,6}]octane (**9f**): mp 94–95 °C (pentane); 40% yield from **2g** (also obtained from the two **3g** isomers); NMR (80) δ 1.05, (s, 1, C_8 *endo*-H), 1.1–1.9 (m, 6), 2.2–2.4 (m, 4, with a sharp s at 2.23 due to C_8 *exo*-H), 7.5–8.0 (m, 5); IR (KBr) 1306, 1296, 1220, 1140, 1080, 990, 960 cm^{-1}; mass spectrum, m/e 248 (M^+), 143, 125, 123, 107, 91. Anal. ($C_{14}H_{16}O_2S$) C, H.

Registry No. **1a**, 67100-44-1; **1b** (Ar = Ph), 81582-87-8; **1b** (Ar = *p*-tolyl), 59555-67-8; **1c** (Ar = Ph), 81582-88-9; **1c** (Ar = *p*-tolyl), 81582-89-0; **1d** (Ar = Ph), 59555-69-0; **1d** (Ar = *p*-tolyl), 81582-90-3; **1e**, 59555-70-3; **1f**, 81582-91-4; **1g**, 81582-92-5; **1h**, 81582-93-6; **2a**, 81582-94-7; **2b** (Ar = Ph), 81582-95-8; **2b** (Ar = *p*-tolyl), 81582-96-9; **2c** (Ar = Ph), 81582-97-0; **2c** (Ar = *p*-tolyl), 81582-98-1; **2d** (Ar = Ph), 81582-99-2; **2d** (Ar = *p*-tolyl), 81583-00-8; **2e**, 81583-01-9; **2f**, 81583-02-0; **2g**, 81583-03-1; **2h**, 81583-04-2; **3a**, 78710-66-4; **3a** 2,4-dinitrobenzoate, 81583-05-3; **3a** mesylate, 81599-94-2; *cis*-**3b** (Ar = Ph), 81583-06-4; *trans*-**3b** (Ar = Ph), 81583-07-5; *cis*-**3b** mesylate (Ar = Ph), 81583-08-6; *trans*-**3b** mesylate (Ar = Ph), 81583-09-7; *cis*-**3b** (Ar = *p*-tolyl), 81583-10-0; *cis*-**3b** 3,5-dinitrobenzoate (Ar = *p*-tolyl), 81583-11-1; *trans*-**3b** (Ar = *p*-tolyl), 81583-12-2; *trans*-**3b** 3,5-dinitrobenzoate (Ar = *p*-tolyl), 81583-13-3; *trans*-**3b** acetate (Ar = *p*-tolyl), 81583-14-4; *cis*-**3b** acetate (Ar = *p*-tolyl), 81583-15-5; *trans*-**3b** propionate (Ar = *p*-tolyl), 81583-16-6; **3c** (Ar = Ph), 81602-31-5; **3c** tosylate (Ar = Ph), 81583-17-7; **3c** (Ar = *p*-tolyl), 81602-32-6; **3d** (Ar = Ph), 81583-18-8; **3d** (Ar = *p*-tolyl), 81583-19-9; **3e**, 81583-20-2; **3f**, 81583-21-3; *trans*-**3g**, 81583-22-4; *cis*-**3g**, 81602-33-7; **3h**, 81583-23-5; **3h** tosylate, 81583-48-4; **4a**, 59555-87-2; **4b**, 59555-86-1; **5a** (Ar = Ph), 81583-24-6; **5a** (Ar = *p*-tolyl), 81583-25-7; **5b** (Ar = Ph), 81583-26-8; **5b** (Ar = *p*-tolyl), 81583-27-9; **5c**, 81583-28-0; **5d**, 81583-29-1; **6a** (Ar = Ph) (diastereomer 1), 81602-34-8; **6a** (Ar = Ph) (diastereomer 2), 81602-35-9; **6b** (Ar = Ph) (diastereomer 1), 81602-36-0; **6b** (Ar = Ph) (diastereomer 2), 81602-37-1; **6b**-*d* (Ar = Ph), 81599-95-3; **6b** (Ar = *p*-tolyl) (diastereomer 1), 81583-30-4; **6b** (Ar = *p*-tolyl) (diastereomer 2), 81602-38-2; **6c** (diastereomer 1), 81602-39-3; **6c** (diastereomer 2), 81602-40-6; *cis*-**7a** (Ar = Ph), 81602-41-7; *cis*-**7a** (Ar = Ph) 3,5-dinitrobenzoate, 81602-42-8; *trans*-**7a** (Ar = Ph), 81602-43-9; *trans*-**7a** (Ar = Ph) 3,5-dinitrobenzoate, 81602-44-0; *cis*-**7b** (Ar = Ph), 81602-45-1; *cis*-**7b**-*3-d* (Ar = Ph), 81583-31-5; *cis*-**7b** (Ar = *p*-tolyl), 81583-32-6; *trans*-**7b** (Ar = *p*-tolyl), 81602-46-2; **7c** (isomer I), 31624-16-0; **7c**-*3′-d* (isomer I), 81583-33-7; **7c** (isomer II), 81602-47-3; **7c**-*3′-d* (isomer II), 81602-48-4; **7c** (isomer III), 81602-49-5; **7c**-*3′-d* (isomer III), 81602-50-8; **7c**-IV (isomer IV), 81602-51-9; **7c**-*3′-d* (isomer IV), 81602-52-0; **8**, 81583-34-8; **8** 2,4-DNP, 81583-35-9; **9a**, 80989-84-0; **9b**, 80989-89-5; **9c** (Ar = *p*-tolyl), 81583-36-0; **9c** (Ar = Ph), 81602-53-1; **9d**, 81583-37-1; **9e**, 81583-38-2; **9f**, 81583-39-3; **10a** (Ar = Ph), 81624-17-1; **10a** (Ar = *p*-tolyl), 81583-40-6; **10b**, 81583-41-7; **10c**, 81583-42-8; **10d**, 81583-43-9; **10e**, 80989-93-1; **10f**, 81583-44-0.