6975-98-0; tryptycene, 477-75-8; fluoranthene, 206-44-0; *cis*-2-pentene, 627-20-3; pentane, 109-66-0; 3,3-dimethyl-1-butene, 558-37-2; 2-methylpentane, 107-83-5; styrene, 100-42-5; octane, 111-65-9; biphenyl, 92-52-4; hexadecane, 544-76-3; triphenylene, 217-59-4; undecane, 1120-21-4.

Supplementary Material Available: Tables containing the names and experimental fusion entropies and enthalpies of the 191 hydrocarbons used in this correlation as well as the values estimated by the group additivity parameters of Table I (21 pages). Ordering information is given on any current masthead page.

Experimental Evidence for the Lack of Stereoselectivity in the Electrophilic Quench of α-Sulfonyl Carbanions

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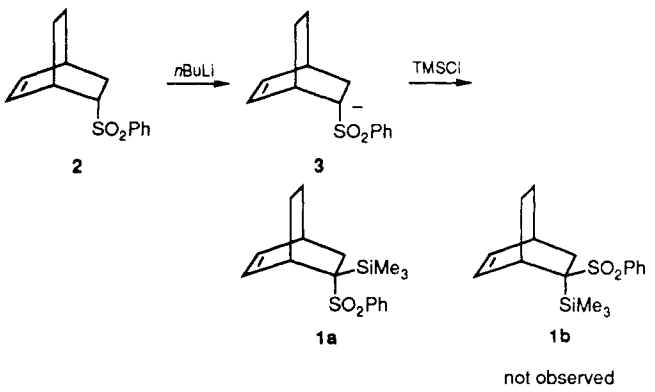
Received July 6, 1989

A series of α-sulfonyl carbanions was generated from the corresponding bridged bicyclic sulfones. These anions were quenched with a variety of electrophiles, and the stereoselectivities of these reactions were examined. Stereochemical assignments were based on X-ray and NMR data. It was found that factors other than the initial stereochemistry of the sulfonyl group dominated any observed stereoselectivity. Deuterium-labeling studies revealed essentially no stereoselectivity in the electrophilic quenches of the symmetrical bicyclo[2.2.2]octane system.

In connection with our interest in developing new synthetic methods utilizing novel aspects of organosilicon and organosulfur chemistry,[1] we prepared the epimeric silylsulfones **1a** and **1b**. The simplest approach appeared to be from the known[2] 5-*endo*-(phenylsulfonyl)bicyclo-[2.2.2]oct-2-ene (**2**) by generation of the α-sulfonyl anion **3** and subsequent quenching with chlorotrimethylsilane ((TMS)Cl).



2 **3** **1a** **1b**

not observed

Indeed Paquette[2] had demonstrated that the anion generated from the epimeric mixture of 1-methoxy-6-*endo*/*exo*-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene could be readily quenched with simple electrophiles. The endo:exo ratio of this epimeric starting material is not specifically reported, although from the preparation it is isolated as a 4.56:1 mixture of endo and exo (sulfonyl group) epimers. The products from these quenching reactions ranged between 2 and 3.7:1 mixtures of endo to exo (sulfonyl group) isomers.[2] In our system, quenching of the carbanion **3** (derived from the single epimer **2**) with (TMS)Cl gave only one product (GC analysis), **1a** or **1b** in 93% isolated yield. Recent calculations at the ab initio level by Wolfe suggest that stereoselectivity should be observed in the quenching of α-lithiosulfones,[3] and he comments that "the very limited experimental data are consistent with this conclusion". It is not feasible to carry out such calculations on systems as large as **3**. However, it is reasonable to anticipate that if the dominant influence controlling the stereochemistry of electrophilic quenching of these carbanions is the sulfonyl group itself, then Wolfe's predictions should apply in the current study. There has been much debate as to the nature of α-sulfonyl anions,[4] especially as to whether the geometry at the α-carbon is planar or pyramidal.[5] The results from most studies on the quenching of α-sulfonyl anions can be explained in terms of either an asymmetrically solvated planar carbanion or a pyramidal carbanion. There are many studies supporting either a planar[6] or pyramidal[10] geometry for the anionic site. However, the

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(1) Williams, R. V.; Sung, C.-L. A. *J. Chem. Soc., Chem. Commun.* **1987**, 590. Williams, R. V.; Ebey, W. J.; Ji, X.; van der Helm, D. *Acta Crystallogr.* **1989**, *B45*, 93. Williams, R. V.; Lin, X. *J. Chem. Soc., Chem. Commun.* **1989**, 1872.
(2) Carr, R. V. C.; Williams, R. V.; Paquette, L. A. *J. Org. Chem.* **1983**, *48*, 4976.
(3) Wolfe, S.; LaJohn, L. A.; Weaver, F. *Tetrahedron Lett.* **1984**, *25*, 2863.
(4) For general reviews on α-sulfonyl carbanions see: Wolfe, S. In *Studies in Organic Chemistry 19: Organic Sulfur Chemistry Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; p 133. Oae, S.; Uchida, Y. In *The Chemistry of Sulphones and Sulphoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; John Wiley and Sons: Chichester, 1988; p 583.
(5) Brown, M. D.; Cook, M. J.; Hutchinson, B. J.; Katritzky, A. R. *Tetrahedron* **1971**, *27*, 593.
(6) For example, see refs 4 and 7-9, and references cited therein.
(7) Corey, E. J.; Lowry, T. H. *Tetrahedron Lett.* **1965**, 793.
(8) Bordwell, F. G.; Branca, J. C.; Johnson, C. R.; Vanier, N. R. *J. Org. Chem.* **1980**, *45*, 3884.
(9) Lett, R.; Chassaing, G.; Marquet, A. *J. Organomet. Chem.* **1976**, *111*, C17.
(10) For example, see: refs 4, 11, and 12, and references cited therein.
(11) Ratajczak, A.; Anet, F. A. L.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 2072.
(12) Bordwell, F. G.; Doomes, E.; Corfield, P. W. R. *J. Am. Chem. Soc.* **1970**, *92*, 2581.

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scope of the majority of these studies was somewhat restricted. In particular, the geometry of the sulfonyl group was frequently locked in a cyclic array.[5,13-15] More recent X-ray structural data support the notion of a pyramidal geometry,[16] while solution-phase NMR results[17] demonstrate relatively rapid inversion of such a pyramidal center (at least in the case of the cyclopropyl system). Ab initio calculations by the Streitwieser group clearly show that for a simple "naked" α-sulfonyl carbanion the planar geometry is 0.57 kcal mol^{-1} more stable than a pyramidal geometry.[18] Streitwieser considered this energy difference to be too small to be of major significance. The situation is reversed when the lithium counterion is included in his calculations, with the ground state now favoring a pyramidal geometry.[18] Similar results were also obtained by Wolfe in his calculations.[3,19] It is interesting to note that the geometry reported for these anionic systems shows a considerable dependence upon solvent and counterion.[4] In the cases of a more naked anion (as is usually observed in the more polar coordinating solvents[8]), there appears to be a trend toward a planar geometry.[18] Due to the wide disparity in experimental conditions (particularly substrate, solvent, and counterion), no general conclusion as to the geometry of the carbanion site is possible. In the present study there is the potential for free rotation about the bicyclic carbon to sulfur (Cα–S) bond in **2**, which is in direct contrast to the systems studied by Katritzky,[5] Durst,[13] De Waard,[14] and Paquette[15] and which should allow for direct determination of any inherent stereochemical control exerted by the sulfonyl group.

For simplicity, throughout this study, the carbanionic system derived from a precursor sulfone is represented as the single pyramidal species resulting from α-proton abstraction with retention of configuration. Of course, as already discussed, the anionic system is much more complex.

In light of the stereospecific (TMS)Cl quench of anion **3**, we decided to test the generality of this observation and determine whether the sulfonyl group is indeed capable of exerting stereochemical control. A series of α-sulfonyl carbanions was generated from rigid bicyclic precursors, and these anions were quenched with various electrophiles. The current study presents experimental results on the observed stereochemical outcome of various α-sulfonyl anion quenching reactions and does not address the question of the geometry of the carbanion sites.

Results and Discussion

The anion **3**, generated by *n*-butyllithium treatment of a solution of sulfone **2** in dry tetrahydrofuran (THF)/hexamethylphosphoramide (HMPA), was quenched with (TMS)Cl. A single product was isolated in 93% yield. The available spectroscopic data (^{1}H and ^{13}C NMR, mass, and infrared spectra) firmly established that the product was **1a** or **1b**, but assignment of stereochemistry with only a single epimer in hand was uncertain. Recourse was therefore made to X-ray crystal structure analysis. These studies unambiguously established that electrophilic quenching had occurred with complete retention of configuration to give **1a** as the sole product.

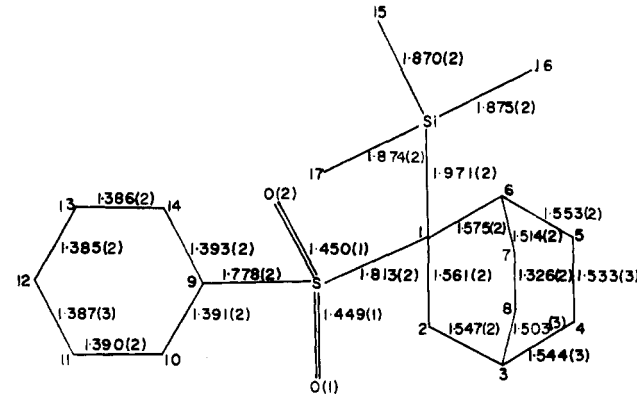


Figure 1. Final bond distances and X-ray atom numbering scheme for **1a**.

The final bond distances and X-ray numbering system for **1a** are shown in Figure 1, and a stereoview is presented in Figure 2. The figures clearly show the phenylsulfonyl group to be endo. There is considerable strain around atom C(1), which is reflected in the unusually large bond distances for this atom and in the torsional angles around the C(1)–Si bond, which are 26° away from an ideal staggered conformation. The torsional angle C(1)–S–C(9)–C(10) is 83° and describes the orientation of the phenyl ring. The three six-membered rings are in boat conformations, and except for the bond distances for C(1), all other bond distances have normal values.

Anion **3** was generated from sulfone **2** under the same conditions as for the (TMS)Cl quench (dry THF/HMPA solution with *n*-butyllithium). Stereoselective quenching of anion **3** resulted when methyl iodide or 1-bromopropane was added to the THF/HMPA solution to give a dominance of the endo sulfonyl product (retention of configuration). The stereochemistry of the products was established by NMR spectroscopy. The most distinctive feature is that the endo (sulfonyl group) epimers exhibited individual signals for each olefinic proton (H-2 and H-3, see the Experimental Section for the conventional numbering system used in describing these bicyclic compounds) whereas the exo epimers displayed a single resonance (multiplet) for both H-2 and H-3. This is, of course, to be expected as a result of the anisotropy associated with the phenylsulfonyl group. Further support for the stereochemical assignments is gained from the observed resonances for the substituents introduced upon electrophilic quench. In the endo (sulfonyl group) epimers the resonances associated with these substituents were consistently found at lower field than the corresponding signals for the exo isomers.[20] Due to the desirability of avoiding the use of the highly toxic HMPA, the (TMS)Cl, MeI, and PrBr quenches were repeated with THF as the sole solvent. The (TMS)Cl reaction still proceeded with complete retention of configuration, and the other reactions continued to be stereoselective. Having established that stereoselectivity is still observed in the absence of the HMPA cosolvent, anion **3** was generated in dry THF and quenched with a variety of electrophiles. The results of these quenches are summarized in Table I.

As can be seen from Table I all of the electrophilic quenches are highly stereoselective. It is interesting to note

(13) Durst, T. *Tetrahedron Lett.* **1971**, 4171.
(14) Kattenberg, J.; De Waard, E. R.; Huisman, H. O. *Tetrahedron* **1974**, *30*, 463.
(15) Paquette, L. A.; Freeman, J. P.; Wyvratt, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 3216.
(16) Hollstein, W.; Harms, K.; Marsch, M.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 846.
(17) Gais, H.-J.; Vollhardt, J.; Lindner, H. J.; Paulus, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1540.
(18) Bors, D. A.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 1397.
(19) Wolfe, S.; Stolow, A.; LaJohn, L. A. *Tetrahedron Lett.* **1983**, 4071.
(20) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982.

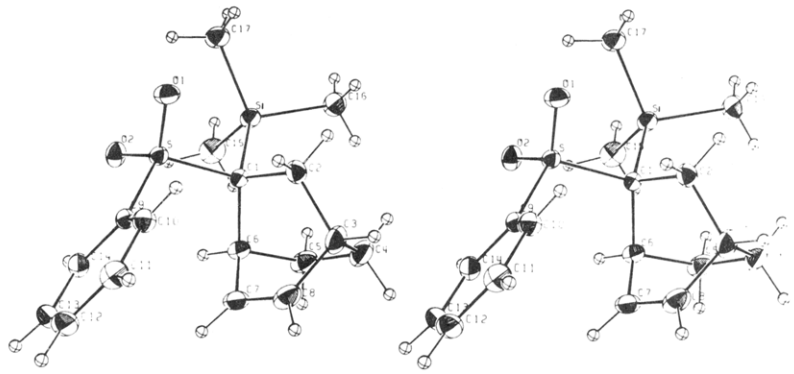
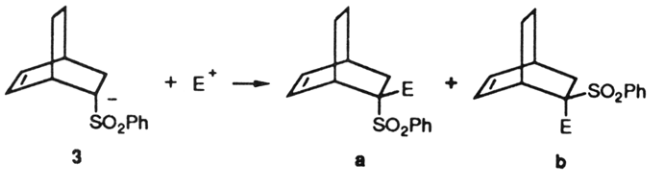


Figure 2. Stereoview of **1a**.

Table I. Stereoselectivity of Electrophilic Quenching of Anion 3



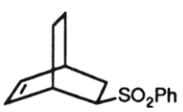
3 a b

electrophile	product endo	product exo	endo exo[a]	yield (%)
(TMS)Cl (HMPA)[b]	**1a**	**1b**	1:0	93
(TMS)Cl[c]	**1a**	**1b**	1:0	86
MeI(HMPA)[b]	**4a**	**4b**	8.3:1	84
MeI	**4a**	**4b**	3.3:1	93
PrBr (HMPA)[b]	**5a**	**5b**	3.6:1	86
PrBr	**5a**	**5b**	1.8:1	83
CH_2=$CHCH_2Br$	**6a**	**6b**	1.5:1	89
Me_2C=$CHCH_2Br$	**7a**	**7b**	16.7:1	89
$PhCH_2Br$	**8a**	**8b**	1:0	92
D_2O	**9a**	**9b**	11.1:1	85
H_2CO	**10a**	**10b**	3.1:1	87
PhCHO	**11a**	**11b**	1:0	85

[a] The endo:exo ratio was determined from vapor-phase chromatography with a mass-selective detector (GC/MS). Similar ratios were obtained from NMR and isolated weights. The stereochemical assignments were based on NMR spectroscopy and the characteristic observation that the exo isomer always had the shorter retention time on GC. [b] These results were obtained with the HMPA cosolvent. [c] In some of the quenches with (TMS)Cl without HMPA cosolvent a second low-intensity Me_3Si– peak was observed at δ 0.0 in the ^1H NMR. This second peak may arise from traces of **1b**.

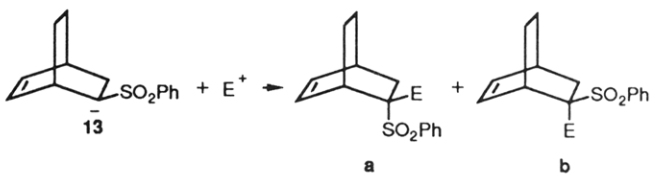
that when the coordinating cosolvent HMPA is used, the quenches are somewhat more stereoselective. This observation perhaps results from the carbanionic center being more naked in the presence of HMPA,[8] with a resultant decrease in the degree of pyramidalization at the anionic center.[18] This could result in an increased conformational control of quenching in which one rotamer (about the Cα–S bond) is preferred.

At this point the question is raised of whether the observed stereoselectivity is a consequence of stereochemical control by the sulfonyl group or a result from control by the unsymmetrical bicyclo[2.2.2]octene nucleus. To address this point, the corresponding exo sulfone **12** was treated in the usual fashion to generate anion **13**, which was once more quenched with a selection of electrophiles (Table II).



12

Table II. Stereoselectivity of Electophilic Quenching of Anion 13



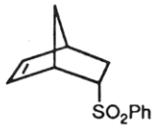
13 a b

electrophile	product[a] endo	product[a] exo	endo:exo	yield (%)
(TMS)Cl	**1a**	**1b**	5:1	87
MeI	**4a**	**4b**	4.8:1	88
D_2O	**9a**	**9b**	5.3:1	88

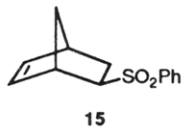
[a] See footnote *a*, Table I.

As is apparent, these electrophilic quenches are also stereoselective. However, the dominant epimer results from *inversion* of configuration. Clearly the observed stereoselectivity in the quenching of these anions derived from both the endo and exo sulfones **2** and **12** must result from control by the bicyclo[2.2.2]octene nucleus. This control perhaps is achieved through the well-known participation of the remote double bond with the carbanionic center.[21]

To further test the stereoselectivity observed upon electrophilic quenching of α-sulfonyl anions, we turned our attention to the norbornyl nucleus. Both the *endo*-**14** and *exo*-**15** norbornenes were examined.



14

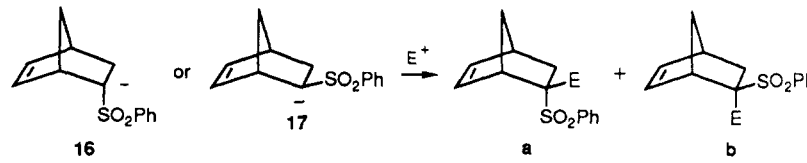


15

The corresponding anions **16** and **17** were generated in the usual fashion with *n*-butyllithium in dry THF. Once more it is apparent (Table III) that the reactions are stereoselective. However, again the stereochemical control is dominated by the unsymmetrical norbornyl nucleus. Once more, the assignment of stereochemistry was made by means of ^1H NMR spectroscopy. As in the case of the bicyclo[2.2.2]octenes the electrophilically introduced substituents resonate at higher field in the exo (sulfonyl group) than the endo isomers.[20] Also of key importance is the observation that the H-6 endo proton is considerably deshielded by the proximate phenylsulfonyl group in the

(21) For example see: Bethell, D. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Ed. Board, Stoddart, J. F., Ed.; Pergamon Press: Oxford, 1979; Vol. 1, p 441. Stille, J. K.; Sannes, K. N. *J. Am. Chem. Soc.* **1972**, *94*, 8494.

Table III. Stereoselectivity of Electrophilic Quenching of Anions 16 and 17

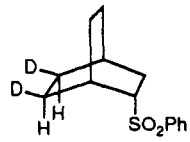


	anion 16				anion 17			
	product				product			
electrophile	endo	exo		yield (%)	endo	exo		yield (%)
MeI	**18a**	**18b**	2.2:1	87	**18a**	**18b**	1.5:1	85
PrBr	**19a**	**19b**	1.3:1	87	**19a**	**19b**	2.9:1	87
D_2O	**20a**	**20b**	3.7:1	90	**20a**	**20b**	2.5:10	92

[a] See footnote *a*, Table I.

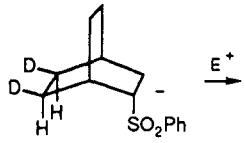
endo compared with the corresponding exo (sulfonyl group) epimers. Similarly the H-6 exo proton resonates at higher field in the endo (sulfonyl group) isomers than the corresponding exo isomers.

In an effort to observe the stereochemical control exerted by the sulfonyl group alone, we considered the essentially symmetrical specifically deuterated bicyclo[2.2.2]octane nucleus **21**.

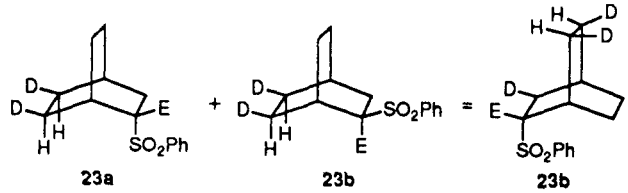


21

The corresponding anion **22** was generated in the usual fashion and quenched with a variety of electrophiles. The products **23a** and **23b** would be enantiomeric if not for the deuterium substitutions. Hence, separation of **23a** and **23b** is clearly nontrivial. However, these epimers can be



22



23a **23b** **23b**

readily distinguished by consideration of their ^{13}C NMR spectra. In **23a** the ethano bridge substituted with deuterium is proximate to the sulfone group whereas the unsubstituted ethano bridge is spatially distant. In **23b** the reverse is true with the deuterium-substituted bridge being removed from the sulfonyl group. Thus, the two ethano bridges have separate distinct resonances in the ^{13}C NMR spectrum, which can be readily identified by their ^{13}C–D couplings. Therefore, starting with the pure endo sulfone **21** it is possible to determine the stereochemical control exerted solely by the sulfonyl group. While it is not possible to accurately establish the ratio of products **23a** to **23b**, consideration of the ^{13}C NMR spectrum allows an estimation of any stereochemical control that was exerted. In each case little stereoselectivity was observed, with both distinct types of ethano bridges being deuterium labeled. Crude estimations based on relative signal intensities suggest an approximate 50:50 ratio of epimers. The electrophiles used in the quenching studies of **22** were chlorotrimethylsilane, methyl iodide, and benzyl bromide. In all cases the yield was 85–90%.

Conclusions

Examination of Tables I and II leads to the general conclusion that no matter which epimeric precursor sulfone, **2** or **12**, is used the resulting anions always undergo electrophilic quench to give a dominance of the sulfonyl group in the endo position. Similar results are observed in Table III for the epimeric sulfones **14** and **15** although the selectivities are lower in the bicyclo[2.2.1] cases. The lower selectivity observed in the bicyclo[2.2.1] compared with the bicyclo[2.2.2] systems is not easily explained. Presumably this results from the nature of the carbanions themselves. Obviously the degree of aggregation and counterion association and the barriers to rotation about the Cα-S bond and to carbanion inversion (if appropriate) all affect the stereoselectivity exhibited in each case. Similarly difficult to rationalize are the seemingly incongruous results for the quenches of anions **16** and **17** with PrBr in which the endo precursor **14** yields less endo (sulfonyl) product **19a** than the exo starting material **15**. Once more, there must be a delicate balance between the various competing processes (aggregation, association, rotation, and inversion). This observed preference for electrophilic attack from the exo face is consistent with the well-known propensity of such bicyclic systems to undergo reactions at the exo face.[22] In addition, for both sets of epimers, **2** and **12** or **14** and **15**, quenching the resultant anionic system with the same electrophile leads to different endo:exo product ratios. This clearly demonstrates that no matter what the geometry of the carbanionic center, the epimeric sulfones, **2** and **12** or **14** and **15**, do not initially give the same carbanionic systems upon treatment with base. In the case of the symmetrical **22** where stereochemical control by the bicyclic framework is not anticipated,[23] little or no stereoselectivity was observed. These results can, of course, be rationalized in terms of relatively rapidly inverting pyramidal geometries or by consideration of asymmetrically solvated planar species. It is important to realize that the rate of equilibration of these α-sulfonyl carbanions may be comparable to the rate of electrophilic quenching. Although our studies

(22) For example see: Thomas, A. F.; Schneider, R. A.; Meinwald, J. *J. Am. Chem. Soc.* **1967**, *89*, 68. Barraclough, P.; Young, D. W. *Tetrahedron Lett.* **1970**, 2293. Tidwell, T. T. *J. Am. Chem. Soc.* **1970**, *92*, 8485. Stille, J. K.; Feld, W. A.; Freeburger, M. E. *J. Am. Chem. Soc.* **1972**, *94*, 8485. Corey, E. J.; Shibasaki, M.; Nicolaou, K. C.; Malmsten, C. L.; Samuelsson, B. *Tetrahedron Lett.* **1976**, 737.

(23) Jindal, S. P.; Sohani, S. S.; Tidwell, T. T. *Tetrahedron Lett.* **1971**, 779.

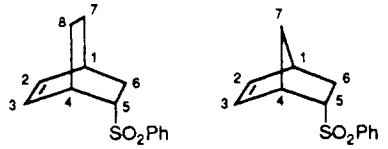
Table IV. Experimental Crystallographic Data for 1a

formula	$C_{17}H_{24}O_2SSi$
MW	320.52
space group	$P2_1/c$ (monoclinic)
cell dimensions	
a	6.570 (1) Å
b	15.389 (3) Å
c	16.260 (4) Å
β	93.26 (2)°
V	1641.3 Å
Z	4
radiation	Mo Kᾱ (λ 0.71069 Å)
temperature	−135 (2) °C
monochromator	graphite crystal
2θ range	1° - 53°
max scan time	60 s
scan angle	(0.70 + 0.20 tan θ)°
monitor reflection checks	
orientation	3 (every 200 reflections)
intensity	3 (every 2 h of X-ray exposure)
variation in monitors	<4%
total no. of data collected	6988
no. of unique data	3377
no. of obsd data with $I > 3\sigma(I)$	2759
R	0.0286
R_w	0.0293

do not shed any light on the geometry of α-sulfonyl carbanions, they do clearly establish the important fact that any stereochemical control exerted by the sulfonyl group in the quench of α-sulfonyl carbanions is weak and easily dominated by other more powerful effects.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1330, ^1H and ^{13}C NMR spectra on a Varian VXR300, and mass spectra on a Hewlett-Packard GC/mass-selective detector (5970A). Melting points were determined in open capillaries and are uncorrected. Microanalyses were performed by Galbraith Laboratories Inc. and by Desert Analytics. Individual proton assignments in the ^1H NMR spectra are based on relative chemical shift and spin/spin coupling data.[20] Often these assignments were made with the aid of two-dimensional NMR spectroscopy (COSY[24]). However, a full analysis[25] of the complex spectra resulting from these bridged bicyclic systems is beyond the scope of the current work. Petroleum ether refers to the fraction with a boiling range of 35–60 °C. The tetrahydrofuran (THF) used in all the experiments was dried by distillation under nitrogen from sodium/benzophenone. All X-ray data were taken on a Nonius CAD 4 diffractometer equipped with a low-temperature nitrogen cryostat. Other experimental data are given in Table IV. The numbering system used for these bicyclic molecules is as follows:



General Procedures for the Generation of the α-Sulfonyl Carbanions. The starting bicyclic sulfones were prepared by the method of Paquette.[2]

Method A (Using Hexamethylphosphoramide Cosolvent). *n*-Butyllithium (1.1 equiv) was added to a stirred cooled (−78 °C) solution of the bicyclic sulfone (1 equiv) in dry THF with approximately 10–40% hexamethylphosphoramide (HMPA) as a cosolvent under nitrogen. The mixture was kept at −78 °C for 15 min, and then the anion was quenched with the appropriate electrophile (1.2–6 equiv). It was allowed to warm slowly to ambient temperature and was kept at this temperature for 1.5 h before being poured into water and extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated in vacuo. The residue was purified by column chromatography on silica gel, eluting with ethyl acetate/petroleum ether mixtures. See Table V for reaction stoichiometries.

Method B. Method B is exactly as method A, omitting the HMPA. In all cases the exo (phenylsulfonyl) isomers eluted first upon column chromatography.

Quenching of Anion 3 with Chlorotrimethylsilane. 5-*endo*-(Phenylsulfonyl)-5-*exo*-(trimethylsilyl)bicyclo[2.2.2]oct-2-ene (1a): white prisms: mp 156–157 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.4 (m, 5 H, Ph), 5.4 (dd, 1 H, J = 2, 8 Hz, olefinic proton), 4.8 (dd, 1 H, J = 1.5, 8 Hz, olefinic proton), 2.9 (m, 1 H, bridgehead), 2.3 (m, 1 H, bridgehead), 1.8–0.8 (m, 6 H, remaining ring protons), 0.4 (s, 9 H, Me_3Si–); ^{13}C NMR ($CDCl_3$), 143.12, 134.33, 133.16, 131.70, 130.64, 128.79, 67.49, 33.26, 31.93, 29.79, 24.63, 23.09, 1.61; IR (KBr) 3060, 2900, 1455, 1290, 1270, 1130, 1080 cm^{-1}; MS m/z (%) 320 (1), 291 (39), 135 (50), 78 (26), 77 (27), 73 (100). Anal. Calcd for $C_{17}H_{24}O_2SSi$: C, 63.70; H, 7.55. Found: C, 63.71; H, 7.22.

Single-Crystal X-ray Analysis of 1a. The space group was determined to be $P2_1/c$, and the compound therefore is a racemate. All intensity data were measured twice on the same crystal and averaged. The sulfur and silicon positions were derived from a Patterson synthesis, and the remaining atom positions, including those for the hydrogen atoms, were obtained from difference Fourier syntheses calculated at various stages of the least-squares refinement. All atoms were refined with anisotropic thermal parameters with the exception of the H atoms, which were refined with isotropic thermal parameters. The final R value was 0.0286, and the crystallographic data, final positional parameters, bond angles, and thermal parameters are available as supplementary material. A final difference Fourier showed no peaks larger than 0.3 e/Å^3, and values of $w(\Delta F)^2$ were evenly distributed with respect to intensity and diffraction angle.

Quenching of Anion 3 or 13 with Methyl Iodide. 5-*endo*-(Phenylsulfonyl)-5-*exo*-methylbicyclo[2.2.2]oct-2-ene (4a): white prisms; mp 117–118 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.75–7.38 (m, 5 H, Ph), 6.20 (dd, 1 H, J = 7, 7 Hz, olefinic H-3), 6.05 (dd, 1 H, J = 7, 7 Hz, olefinic H-2), 2.60 (m, 1 H, bridgehead H-1), 2.50 (m, 1 H, bridgehead H-4), 2.15 (dm, 1 H, J = 13 Hz, H-6 endo), 1.73 (m, 1 H, H-8 syn), 1.35 (s, 3 H, Me–), 1.32–1.00 (m, 4 H); ^{13}C NMR ($CDCl_3$) 136.9, 134.2, 133.6, 131.3, 130.7, 129.0, 66.6, 36.9, 35.1, 30.9, 24.8, 23.5, 22.2; IR (KBr) 3050, 2930, 1445, 1270, 1140 cm^{-1}; MS, m/z (%) 121 (68.5), 93 (100), 79 (33.7), 77 (39.8). Anal. Calcd for $C_{15}H_{18}SO_2$: C, 68.67; H, 6.91. Found: C, 68.66; H, 6.73.

5-*exo*-(Phenylsulfonyl)-5-*endo*-methylbicyclo[2.2.2]oct-2-ene (4b): white prisms, mp 106–107 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.80–7.40 (m, 5 H, Ph), 6.17 (m, 2 H, olefinic), 2.61–2.44 (m, 4 H), 1.70 (m, 1 H), 1.35 (m, 1 H), 1.20 (m, 1 H), 1.05 (m, 1 H), 0.97 (s, 3 H, Me–); ^{13}C NMR ($CDCl_3$) 137.5, 134.4, 134.1, 133.6, 130.1, 129.1, 67.2, 36.2, 35.2, 30.7, 27.2, 23.2, 22.6; IR (KBr) 3045, 2950, 1447, 1287, 1142 cm^{-1}; MS, m/z (%) 121 (85.6), 93 (100), 79 (35.6), 77 (41.5). Anal. Calcd for $C_{15}H_{18}SO_2$: C, 68.67; H, 6.91. Found: C, 68.84; H, 6.91.

Quenching of Anion 3 or 13 with 1-Bromopropane. 5-*endo*-(Phenylsulfonyl)-5-*exo*-*n*-propylbicyclo[2.2.2]oct-2-ene (5a): white prisms; mp 110.5–111 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.75–7.20 (m, 5 H, Ph–), 6.18 (dd, 1 H, J = 7, 7 Hz, olefinic H-3), 5.95 (dd, 1 H, J = 7, 7 Hz, olefinic H-2), 3.06 (m, 1 H, bridgehead H-1), 2.54 (m, 1 H, bridgehead H-4), 2.17 (dm, 1 H, J = 11 Hz, H-6 endo), 1.60–1.85 (m, 3 H), 1.30–1.50 (m, 3 H), 1.0–1.28 (m, 3 H), 0.73 (t, 3 H, J = 5.3 Hz, Me–); ^{13}C NMR ($CDCl_3$) 139.1, 133.8, 133.4, 132.6, 130.1, 128.9, 71.0, 41.6, 38.8, 32.0, 30.5, 23.2, 22.7, 18.6, 15.0; IR (KBr) 3055, 2960, 1471, 1445, 1285, 1140 cm^{-1}; MS, m/z (%) 149 (42.8), 120 (31.7), 105 (16), 91 (100), 79 (53.6), 78 (26), 77 (47.5). Anal. Calcd for $C_{17}H_{22}SO_2$: C, 70.30; H, 7.64. Found: C, 70.46; H, 7.62.

5-*exo*-(Phenylsulfonyl)-5-*endo*-*n*-propylbicyclo[2.2.2]oct-2-ene (5b): white prisms; mp 102–103 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.80–7.17 (m, 5 H, Ph–), 6.20 (m, 2 H, olefinic), 3.10 (m, 1 H, bridgehead H-1), 2.61 (m, 1 H, bridgehead, H-4), 2.50–2.39 (m, 2 H), 1.75 (m, 1 H), 1.55 (m, 1 H), 1.40–0.75 (m, 6 H), 0.53 (t, 3 H, J = 6 Hz, Me–); ^{13}C NMR ($CDCl_3$) 139.8, 134.5, 133.5, 129.2, 71.4, 42.7, 36.9, 33.0,

(24) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

(25) Abraham, R. J.; Fisher, J. *Magn. Reson. Chem.* **1985**, *23*, 856.

Table V. Reaction Stoichiometries

sulfone (mmol)	THF (mL)	HMPA (mL)	BuLi (mmol)	electrophile (mmol)	products (% yield)	
2 (14)	35	3	16	(TMS)Cl (16.6)	**1a** (93)	
2 (2)	8	0	2.22	(TMS)Cl (3.1)	**1a** (86)	
2 (0.806)	2	1.5	0.89	MeI (4.8)	**4a** (73)	**4b** (11)
2 (0.806)	3.5	0	0.89	MeI(4.8)	**4a** (73)	**4b** (19.9)
2 (0.806)	2	1.5	0.89	PrBr (5)	**5a** (67.2)	**5b** (18.8)
2 (0.806)	3.5	0	0.89	PrBr (5)	**5a** (54.1)	**5b** (29.1)
2 (0.806)	3.5	0	0.89	Allyl-Br (5.78)	**6a** (57)	**6b** (32)
2 (0.806)	3.5	0	0.89	Me_2allyl-Br (1.6)	**7a** (89)	
2 (0.806)	3.5	0	0.89	$PhCH_2Br$ (2.5)	**8a** (92)	
2 (0.806)	3.5	0	0.89	D_2O (15)	**9a:9b** 100:9 (85)	
2 (0.806)	8	0	0.89	HCHO (excess)	**10a:10b** 3:1 (87)	
2 (0.806)	3.5	0	0.89	PhCHO (3)	**11a** (85)	
12 (0.806)	3.5	0	0.89	(TMS)Cl (4)	**1a:1b** 5:1 (87)	
12 (0.806)	3.5	0	0.89	MeI (4.8)	**4a** (72.7)	**4b** (15.3)
12 (0.806)	3.5	0	0.89	D_2O (5.5)	**9a:9b** 100:19 (88)	
14 (0.806)	3.5	0	0.89	MeI (8)	**18a** (48.4)	**18b** (38.5)
14 (0.806)	3.5	0	0.89	PrBr (5)	**19a** (68.2)	**19b** (18.6)
14 (0.806)	3.5	0	0.89	D_2O (25)	**20a:20b** 100:25 (90)	
15 (0.806)	3.5	0	0.89	MeI (4.8)	**18a** (54)	**18b** (31)
15 (0.806)	3.5	0	0.89	PrBr (5)	**19a** (64.9)	**19b** (22.1)
15 (0.806)	3.5	0	0.89	D_2O (5.5)	**20a:20b** 100:40 (92)	

30.5, 24.2, 22.3, 17.8, 14.6; IR (KBr) 3050, 2900, 1585, 1450, 1275, 1140 cm^{-1}; MS, *m/z* (%) 149 (36.8), 120 (38.2), 105 (23.8), 91 (106), 79 (44.9), 78 (26.7), 77 (41.3). Anal. Calcd for $C_{17}H_{22}SO_2$: C, 70.30; H, 7.64. Found: C, 70.16; H, 7.71.

Quenching of Anion 3 with Allyl Bromide. 5-*endo*-(Phenylsulfonyl)-5-*exo*-prop-2-enylbicyclo[2.2.2]oct-2-ene (6a): white prisms; mp 45.5–46.5 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.74–7.18 (m, 5 H, Ph–), 6.16 (dd, 1 H, *J* = 7.0, 7.0 Hz, olefinic H-3), 6.07 (m, 1 H, propenyl olefinic), 5.99 (dd, 1 H, *J* = 7.0, 7.0 Hz, olefinic H-2), 5.03 (dd, 1 H, *J* = 10.3, 1.0 Hz, propenyl olefinic), 4.97 (dd, 1 H, *J* = 17.5, 1.0 Hz, propenyl olefinic), 2.94 (m, 1 H, bridgehead H-1), 2.58 (m, 2 H), 2.29 (m, 1 H), 2.11 (m, 1 H), 1.81 (m, 1 H), 1.38–0.97 (m, 4 H); ^{13}C NMR ($CDCl_3$) 139.1, 134.3, 133.8, 133.6, 132.3, 130.5, 128.9, 118.3, 70.3, 42.5, 37.5, 32.7, 30.5, 22.9, 22.5; IR (KBr) 3050, 2930, 1445, 1285, 1140 cm^{-1}; MS, *m/z* (%) 118 (55.2), 117 (100), 91 (82.9), 79 (34.6), 77 (72.7). Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.80; H, 6.99. Found: C, 70.56; H, 7.12.

5-*exo*-(Phenylsulfonyl)-5-*endo*-prop-2-enylbicyclo[2.2.2]oct-2-ene (6b): white prisms; mp 75–76 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.80–7.17 (m, 5 H, Ph–), 6.18 (m, 2 H, olefinic H-1 and H-2), 5.83 (m, 1 H, propenyl olefinic), 4.93 (dd, 1 H, *J* = 7.2, 1.0 Hz, propenyl olefinic), 4.78 (dd, 1 H, *J* = 10.3, 1.0 Hz propenyl olefinic), 3.00 (m, 1 H, bridgehead, H-1), 2.62 (m, 1 H, bridgehead, H-4), 2.47 (m, 2 H), 2.08 (m, 1 H), 1.76 (m, 2 H), 1.30–1.00 (m, 3 H); ^{13}C NMR ($CDCl_3$) 139.8, 134.2, 133.9, 133.7, 129.7, 129.2, 118.3, 70.8, 44.1, 35.8, 33.9, 30.6, 24.0, 22.3; IR (KBr) 3050, 2900, 1576, 1465, 1443, 1287, 1142 cm^{-1}; MS, *m/z* (%) 119 (40.5), 118 (58.6), 117 (100), 91 (78.9), 79 (31.3), 78 (21.6), 77 (62.6). Anal. Calcd for $C_{17}H_{20}O_2S$: C, 70.80; H, 6.99. Found: C, 70.82; H, 7.12.

Quenching of Anion 3 with Dimethylallyl Bromide. 5-*endo*-(Phenylsulfonyl)-5-*exo*-(3-methylbut-2-enyl)bicyclo[2.2.2]oct-2-ene (7a): oil; ^1H NMR ($CDCl_3$, TMS) δ 7.75–7.15 (m, 5 H, Ph–), 6.24 (dd, 1 H, *J* = 5.2, 5.2 Hz, olefinic H-3), 6.06 (dd, 1 H, *J* = 5.2, 5.2 Hz, olefinic H-2), 5.20 (m, 1 H, butenyl olefinic), 2.95 (m, 1 H, bridgehead H-4), 2.57 (m, 1 H, bridgehead H-4) 2.50 (m, 1 H), 2.20 (m, 2 H), 1.65 (m, 1 H), 1.55 (s, 3 H, Me–), 1.40 (s, 3 H, Me–), 1.39–1.03 (m, 4 H); ^{13}C NMR ($CDCl_3$) 138.9, 133.9, 133.7, 133.5, 132.5, 130.4, 128.7, 119.4, 70.0, 37.9, 37.2, 32.6, 30.6, 26.3, 23.2, 22.6, 18.2; IR (film) 3045, 2900, 1580, 1430, 1371, 1280, 1135 cm^{-1}; MS, *m/z* (%) 174 (19.9), 146 (36.0), 131 (100), 95 (26.3), 91 (48.4), 79 (26.3), 78 (20.6), 77 (47.8). Anal. Calcd for $C_{19}H_{24}O_2S$: C, 72.11; H, 7.64. Found C, 72.03; H, 7.77.

Quenching of Anion 3 with Benzyl Bromide. 5-*endo*-(Phenylsulfonyl)-5-*exo*-benzylbicyclo[2.2.2]oct-2-ene (8a): white needles; mp 142–143 °C (from ethyl acetate/petroleum ether); ^1H NMR ($CDCl_3$, TMS) δ 7.52–7.14 (m, 10 H, aromatic), 5.96 (dd, 1 H, *J* = 6, 6 Hz, olefinic H-3), 5.86 (dd, 1 H, *J* = 6, 6 Hz, olefinic H-2), 3.32 (d, 1 H, *J* = 15 Hz, benzylic), 3.25 (d, 1 H, *J* = 15 Hz, benzylic), 2.88 (m, 1 H, bridgehead H-1), 2.53 (m, 1 H, bridgehead H-4), 2.27 (dm, 1 H, *J* = 12 Hz, H-6 exo), 2.09 (m, 1 H), 1.52 (dm, 1 H, *J* = 12 Hz, H-6 endo), 1.32–1.16 (m, 3 H); ^{13}C NMR ($CDCl_3$) 139.7, 137.0, 133.1, 131.3, 130.8, 128.5, 128.4, 127.2, 76.9, 73.4, 42.3, 36.2, 34.7, 31.3, 30.3, 24.0, 23.3; IR (KBr) 3090, 3045, 2940, 1596, 1490, 1440, 1285, 1270, 1130 cm^{-1}. Anal. Calcd for $C_{21}H_{22}SO_2$: C, 74.52; H, 6.55. Found: C, 74.69; H, 6.60.

Quenching of Anion 3 or 13 with D_2O. Gas chromatographic analysis revealed an endo:exo ratio (sulfonyl group) **9a:9b** of 100:9.

Quenching of Anion 3 with Formaldehyde. After the usual workup, the crude product was purified by direct crystallization to give an inseparable epimeric mixture of the 5-*endo*/*exo*-(phenylsulfonyl)-5-*exo*/*endo*-hydroxymethylbicyclo[2.2.2]oct-2-ene: **10a:10b** = 3:1, 0.195 g (0.7 mmol, 87%); ^1H and ^{13}C NMR, IR, and mass spectra, consistent for this mixture. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.78; H, 6.50.

Quenching of Anion 3 with Benzaldehyde. 5-*endo*-(Phenylsulfonyl)-5-*exo*-(hydroxybenzyl)bicyclo[2.2.2]oct-2-ene (11a) was isolated as a mixture of diastereomers; 0.24 g (0.69 mmol, 85%); white prisms; mp 138–148 °C (from ethyl acetate/pentane) ^1H and ^{13}C NMR, IR, and mass spectra, consistent for this mixture. Anal. Calcd for $C_{21}H_{22}O_3S$: C, 71.15; H, 6.25. Found C, 71.09; H, 6.37.

Quenching of Anion 13 with Chlorotrimethylsilane. After the usual workup, the crude material was purified by chromatography (silica, petroleum ether gradually increasing polarity to 10% ethyl acetate/petroleum ether) to give an inseparable mixture of epimers **1a** and **1b**:5:1; 0.224 g (0.7 mmol, 87%); ^1H and ^{13}C NMR, IR, and mass spectra, consistent for this mixture. Anal. Calcd for $C_{17}H_{24}O_2SSi$: C, 63.70; H, 7.55. Found: C, 63.47; H, 7.65.

Quenching of Anion 16 or 17 with Methyl Iodide. 5-*endo*-(Phenylsulfonyl)-5-*exo*-methylbicyclo[2.2.1]hept-2-ene (18a): white prisms; mp 129–130 °C (from ethyl acetate/pentane); ^1H NMR ($CDCl_3$, TMS) δ 7.85–7.15 (m, 5 H, Ph–) 6.26 (m, 1 H, olefinic H-3), 6.17 (m, 1 H, olefinic H-2), 2.90 (m, 1 H, bridgehead H-1), 2.70 (m, 1 H, bridgehead H-4), 2.05 (dm, 1 H, *J* = 12 Hz, H-6 endo), 1.65 (m, 1 H, H-6 exo), 1.40 (m, 1 H, H-7 syn), 1.35 (s, 3 H, Me–), 1.13 (m, 1 H, H-7 anti); IR (KBr) 3072, 2960, 1587, 1453, 1343, 1301, 1150, 1135, 1087; MS, *m/z* (%) 248 (1.9), 183 (60.1), 107 (24.2), 91 (41.9), 79 (66.1), 77 (34.2), 66 (100), 65 (20.8). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.50. Found: C, 67.41; H, 6.38.

5-*exo*-(Phenylsulfonyl)-5-*endo*-methylbicyclo[2.2.1]hept-2-ene (18b): white prisms; mp 99–100 °C (from ethyl acetate/pentane); ^1H NMR ($CDCl_3$, TMS) δ 7.85–7.15 (m, 5 H, Ph–) 6.20 (m, 1 H, olefinic H-2), 5.95 (m, 1 H, olefinic H-3), 3.00 (s, 1 H, bridgehead H-4), 2.95 (s, 1 H, bridgehead H-1), 2.55 (dd, 1 H, *J* = 9, 2 Hz, H-6 exo), 2.35 (d, 1 H, *J* = 9 Hz, H-7 syn), 1.35 (m, 1 H, H-7 anti), 1.10 (s, 3 H, Me–), 0.95 (dd, 1 H, *J* = 9, 2 Hz, H-6 endo); ^{13}C ($CDCl_3$) 140.4, 138.1, 135.6, 133.7, 130.3, 129.2, 70.6, 49.6, 48.8, 43.4, 35.8, 23.4; IR (KBr) 3075, 2960, 1586, 1452, 1300, 1151, 1072; MS, *m/z* (%) 183 (20.8), 167 (1.3), 107 (70.7), 91 (67.5), 79 (100), 78 (31.9), 77 (47.2), 66 (88.5), 65 (29.8); found M^+ 247.87,

$C_{14}H_{16}O_2S$ requires M 248.09.

Quenching of Anion 16 or 17 with 1-Bromopropane. 5-*endo*-(Phenylsulfonyl)-5-*exo*-*n*-propylbicyclo[2.2.1]hept-2-ene (19a): white prisms; mp 65–66 °C (from ethyl acetate/pentane); ^{1}H NMR ($CDCl_3$, TMS) δ 7.79–7.17 (m, 5 H, Ph–), 6.23 (dd, 1 H, J = 3.3, 2.5 Hz, olefinic H-3), 6.16 (dd, 1 H, J = 3.3, 2.5 Hz olefinic H-2), 3.09 (s, 1 H, bridgehead H-4), 2.87 (s, 1 H, bridgehead H-1), 2.00 (dd, 1 H, J = 12.8, 2.2 Hz, H-6 endo) 1.60–1.20 (m, 7 H), 0.60 (t, 3 H, J = 7.2 Hz, Me–); ^{13}C NMR ($CDCl_3$) 140.2, 138.4, 134.4, 133.4, 129.3, 129.1, 74.2, 49.2, 48.5, 43.2, 41.1, 37.7, 18.2, 14.8; IR (KBr) 3037, 2960, 1589, 1452, 1287, 1147, 1089; MS, m/z (%) 211 (10.5), 134 (17.2), 105 (34.5), 92 (20.1), 91 (59.9), 79 (26.5), 78 (21.3), 77 (29.6), 66 (100), 65 (28.2), 64 (26.4). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.51; H, 7.54.

5-*exo*-(Phenylsulfonyl)-5-*endo*-*n*-propylbicyclo[2.2.1]-hept-2-ene (19b): white prisms; mp 107–108 °C (from ethyl acetate/pentane); ^{1}H NMR ($CDCl_3$, TMS) δ 7.83–7.18 (m, 5 H, Ph–), 6.23 (m, 1 H, olefinic H-2), 6.05 (m, 1 H, olefinic H-3), 3.43 (s, 1 H, bridgehead H-4), 2.88 (s, 1 H, bridgehead H-1), 2.59 (dd, 1 H, J = 9.8, 1.8 Hz, H-6 exo), 2.34 (d, 1 H, J = 8 Hz, H-7 anti), 1.60 (m, 1 H), 1.38 (d, 1 H, J = 8 Hz, H-7 syn), 1.19 (m, 3 H) 0.90 (dm, 1 H, J = 10 Hz, H-6 endo), 0.59 (t, 3 H, J = 6.2 Hz, Me–); ^{13}C NMR ($CDCl_3$) 141.0, 139.7, 135.5, 133.5, 129.4, 129.3, 75.2, 48.4, 47.8, 43.0, 40.3, 37.3, 18.9, 14.8; IR (KBr) 3070, 2960, 1587, 1475, 1450, 1308, 1286, 1246, 1089; MS, m/z (%) 134 (22.7), 105 (36.3), 92 (22%), 91 (63.9), 79 (24.9), 78 (25.4), 77 (24.0), 66 (100), 65 (22.5), 64 (24.3). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29. Found: C, 69.41; H, 7.44.

Quenching of Anion 16 or 17 with D_2O. After the usual workup the ratio of **20a**:**20b** (100:27) was determined by gas chromatographic analysis.

2-(Phenylsulfonyl)[5,6-$^2H_2$]bicyclo[2.2.2]octane (21). A stirred solution of 5-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (0.2 g, 0.806 mmol) in ethyl acetate (15 mL) was subjected to catalytic deuteration (Pd on C 10%, 20 mg) at lecture bottle pressure and ambient temperature for 3 h. The mixture was filtered through Celite and the filtrate evaporated in vacuo. The solid residue was purified by recrystallization (ethyl acetate/petroleum ether) to give the pure sulfone (**21**) as white prisms: mp 58–59 °C; 0.193 g (0.77 mmol, 95%); ^{1}H NMR ($CDCl_3$, TMS) δ 7.92–7.26 (m, 5 H, Ph–), 3.16 (m, 1 H H-2), 2.24 (d, 1 H, J = 12 Hz, bridgehead H-1), 2.07 (m, 2 H), 1.72–1.35 (m, 6 H); ^{13}C NMR ($CDCl_3$) 139.1, 133.4, 129.1, 128.4, 62.4, 26.9, 26.7, 24.5, 24.4 (t, J = 19.4 Hz), 24.3, 24.0, 20.8, (t, J = 19.7 Hz); IR (KBr) 3032, 2950, 2872, 2188, 1452, 1305, 1280, 1238, 1154, 1092 cm^{-1}; MS, m/z (%) 143 (10), 111 (100), 77 (25), 69 (23), 68 (41), 67 (20). Anal. Calcd for $C_{14}H_{16}D_2O_2S$: C, 66.63; H(D), 7.19. Found: C, 66.95; H(D), 7.25.

Quenching of Anion 22 with Chlorotrimethylsilane, Methyl Iodide, and Benzyl Bromide. Method B was followed in each case with 1.1 equiv of butyllithium, sulfone **21**, and quenching with 3–5 equiv of the electrophiles. After the usual workup and purification by chromatography (silica, petroleum ether gradually increasing polarity to 7.5% ethyl acetate/petroleum ether), all spectroscopic data were consistent with the respective products. Detailed analysis of the ^{13}C NMR revealed that each purified product was a mixture of endo and exo products. While it was impossible to accurately determine the epimeric ratio, crude estimations based on relative ^{13}C NMR peak heights suggest that little or no stereoselectivity is observed in these reactions.

Acknowledgment. The award of a NATO collaborative grant to R.V.W. and P.C.B.P. is gratefully acknowledged.

Supplementary Material Available: Tables VI–IX of final atomic positions, bond angles, hydrogen atom parameters, and anisotropic thermal parameters for **1a** (4 pages). Ordering information is given on any current masthead page.

Mechanistic Interpretation of Reactions with Opposing Signs of Field and Resonance Reaction Constants in the Dual Substituent Parameter Treatments of Taft, Yukawa-Tsuno, and Godfrey

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Received June 26, 1989

Fourteen reactions with opposing signs of field and resonance reaction constants ρ_F and ρ_R in Taft's dual substituent parameters (DSP) treatment are discussed mechanistically and compared, in part, with the corresponding evaluation by the DSP equations of Yukawa and Tsuno and of Godfrey. The experimental data are fitted best by Taft's treatment. Godfrey's claim that meta- and para-substituted benzene derivatives yield the same reaction constants ρ and λ cannot be verified for the dediazoniation of arenediazonium ions. In addition to Taft's explanation for opposing signs of ρ_F and ρ_R, namely, positive charge moving closer to the substituent in going from reactant to transition state, it is shown here that a series of reactions (dediazoniation, azide decomposition, addition reactions of aryl cations and of singlet carbenes) is characterized by concerted σ bond formation and back donation of π electrons between the two reagents.

Dual substituent parameter (DSP) relationships allow the separation of the influence of field (or inductive) and resonance effects of substituents on chemical reactivities and physical properties (e.g., electronic and NMR spectra, etc.) of organic compounds. In this paper we will discuss the rates of a series of reactions that show opposing influence of field and resonance effects and then use this series to compare three DSP relationships: those of Taft,[1] of Yukawa and Tsuno,[2] and the recent proposal of Godfrey.[3]

(1) (a) Taft, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 1045. (b) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.
(2) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965, 971; **1966**, *39*, 2274.
(3) Fadhil, G. F.; Godfrey, M. *J. Chem. Soc., Perkin Trans. II* **1988**, 133. Godfrey, M. *J. Chem. Soc., Perkin Trans. II* **1988**, 138.

0022-3263/90/1955-3846$02.50/0