Table X[a]

no.	δ (ppm)	J, Hz	S value	assignment
A	0.79 (d)	~12	1.94	
B	0.95 (d)	~12	0.75	H^5 exo or endo
C	1.03 (dd)	~10, ~2	0.60	or H^6 exo or
D	1.19 (dd)	~10, ~2	0.00	endo
E	1.55 (m)	~2, ~2, ~2.9, ~2.9	0.30	H^7 anti and syn
F	2.50 (d)	~2.9	1.13	H^4
G	2.65 (d)	~2.9	1.93	H^1 (=H^d)
H	2.72 (d)	9.77	0.83	H^3 (=H^c)
I	2.99 (dd)	9.77, 10.38	1.01	H^2 (=H^b)
J	3.50 (s)		0.14	OCH_3
K	5.42 (d)	10.38	3.30	H^a
L	6.14 (d)	9.16	0.50	$NC_6H_4OCH_3$
M	6.29 (d)	9.16	0.74	

[a] The best fit of experimental S values with those of calculated values (Yamazaki A. *Kagaku (Kyoto)* **1974**, *29*, 349; Roberts J. D., Hawkes G. E., Roberts A. W., Roberts D. W., *Tetrahedron* **1974**, *30*, 1833.) was found when the exo-anti configuration was assumed (correlation coefficient = 0.87). The correlation coefficients for other configurations were smaller (for exo-syn 0.78 and for endo-anti 0.77).

70%. The physical data were identical with that reported previously.[1b]

A benzene solution of **1a** (400 mg) and dimethyl maleate (1 g) was irradiated through a 1-cm $CuSO_4$ filter for 10 h. Solvent and olefin were distilled off at a reduced pressure. Recovered **1a**, **5a**, and **5b** were separated by Kugelrohr distillation at 0.001 torr. Compound **5a** was distilled at 140 °C and **5b** was distilled at 150–170 °C.

Estimation of Electron Affinities of 1b and 2a. Electron affinities of **1b** and **2a** were estimated by using the following equation.[17] $h\nu_j - h\nu_i = EA_i - EA_j$; $h\nu$ is the energy of the longest wavelength transition of the CT absorption, EA is electron affinity, and subscript i denotes the sample and j the reference. The concentration of hydroquinone dimethyl ether was 0.5 M and of **2a** and **1b** 1 mM. The solution of **2a** or **1b** without the donor was placed in the reference. Reference acceptor was 1 mM of 1,4-naphthoquinone. The CT band appeared at 445 nm, 418 nm, 418 nm respectively for 1,4-naphthoquinone, **2a**, and **1b**. By the use of the electron affinity of 1,4-naphthoquinone (1.26 eV),[9a] the electron affinities of **2a** and **1b** were obtained as 1.08 eV.

Reactivity. Quantum yields were measured by using a ferrioxalate actinometer in a benzene solution of a known amount of olefin concentration and 1 mM of **1** or **2**. Quantum yields were dependent upon the amount of olefins in the reacting solutions and were measured at the olefin concentration of 20, 50, 80, 160, and 320 mM. Irradiation was undertaken in a merry-go-round by using 313 nm light for 1 h in the case of **1b** or for 40–80 h in the cases of **2a**. The amounts of cycloadducts were determined by HPLC with a column of μ-Porasil analytical and 5%–20% ether–hexane as eluents. Conversion did not exceed 10%.

Registry No. **1a**, 53948-58-6; **1b**, 13369-47-6; **2a**, 79060-54-1; **2b**, 79060-50-7; **5a**, 63689-05-4; **5b**, 87420-83-5; **5c** (isomer 1), 87373-38-4; **5c** (isomer 2), 87420-85-7; **5d**, 87420-84-6; **6a**, 87373-39-5; **6b**, 87373-40-8; **6c**, 87373-41-9; **6d**, 87373-42-0; **6e**, 87373-43-1; **6f**, 87373-44-2; **6g**, 87420-86-8; **6h**, 87373-45-3; **6i**, 87420-87-9; **6j**, 87420-88-0; **6k**, 87373-46-4; norbornene, 498-66-8; α-methylstyrene, 98-83-9; methyl acrylate, 96-33-3; dimethyl acrylate, 624-48-6; dimethyl fumarate, 624-49-7; 1,3-pentadiene, 504-60-9; acrylonitrile, 107-13-1.

(17) (a) Batley, M.; Lyons. *Nature (London)* **1962**, *196*, 573. (b) Davis, K. M.; Hammond, R. R.; Peover, M. E. *Trans. Faraday Soc.* **1965**, *61*, 1516. (c) Farragher, A. L.; Page, F. M. *Ibid.* **1966**, *62*, 3072.

(18) Jackman L. M.; Sternhell S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: Oxford, 1969; p 289.

(19) Shift reagent experiments were performed on a JEOL JNM-FX400 400-MHz ^1H NMR apparatus with $Eu(fod)_3$ as a shift reagent. The results are given in Table X.

Dienophilic Properties of Phenyl Vinyl Sulfone and *trans*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethylene. Their Utilization as Synthons for Ethylene, 1-Alkenes, Acetylene, and Monosubstituted Alkynes in the Construction of Functionalized Six-Membered Rings via [4 + 2] π Cycloaddition Methodology

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Useful procedures for effecting the indirect capture of ethylene, acetylene, 1-alkenes, and monosubstituted alkynes in Diels–Alder cycloadditions have been developed. In the first sequence, phenyl vinyl sulfone is shown to enter into [4 + 2] π reactions as a moderately reactive dienophile and to do so with very good regioselectivity. The resulting adducts can be directly desulfonated or alkylated prior to such reduction. A wide range of functional groups can be appended in this fashion at a specific locus within the newly formed six-membered ring. When the analogous chemistry is applied to *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene (**2**), adducts result which undergo ready fluoride ion induced elimination with efficient introduction of a double bond. The use of **2** and its d_2 derivative is highlighted by the synthesis of several functionalized dibenzobarrelenes.

The low reactivity of unadorned alkenes and alkynes as dienophilic reagents ranks as one of the foremost limitations of Diels–Alder cycloaddition chemistry. To achieve the [4 + 2] π condensation of ethylene to butadienes, temperatures of 175 °C and pressures of 6000 psi or more are required.[1,2] Somewhat less forcing conditions are necessary for allyl compounds,[3,4] although yields are often little improved. More constrained olefins have been reported to react with highly activated dienes with greater facility,[5,6] although such behavior is hardly typical. The

(1) (a) Wheeler, R. V.; Wood, W. L. *J. Chem. Soc.* **1930**, 1819. (b) Jostel, L. M.; Butz, L. W. *J. Am. Chem. Soc.* **1941**, *63*, 3350.

(2) Bartlett, P. D.; Schueller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6071.

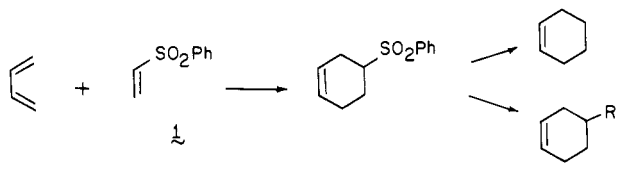
(3) Huisgen, R.; Grashey, R.; Sauer, J. In "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; Chapter 11.

(4) (a) Alder, K.; Rickert, H. F. *Chem. Ber.* **1938**, *71*, 373. (b) Alder, K.; Windenmuth, E. *Ibid.* **1938**, *71*, 1939. (c) Alder, K.; Rickert, H. F. *Justus Liebigs Ann. Chem.* **1939**, *543*, 1.

0022-3263/83/1948-4976$01.50/0

safety hazards associated with the handling of acetylene at elevated temperatures and pressures are well-known[7] and should be avoided. Probably the most important factor contributing to the sluggishness of these reactions is the unfavorable π donor–acceptor complementarity between diene and dienophile which inhibits smooth HOMO–LUMO electron flow.

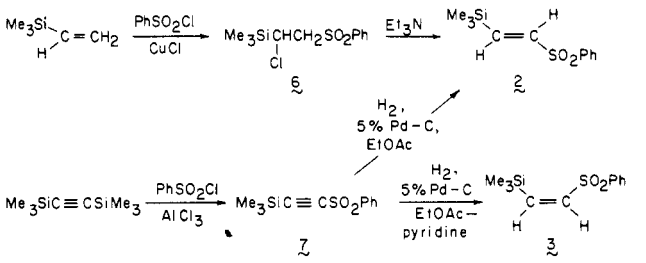
Against this backdrop, work was initiated in this laboratory in 1978 to develop a general, high-yielding, indirect solution to this overall problem. A number of clever procedures had previously been devised to achieve acetylene equivalency,[8-14] but these processes either require the isolation of intermediates followed by functional group manipulation or suffer from modest overall yields and/or undesirable side reactions. To facilitate frontier orbital interaction, we have made recourse to phenylsulfonyl substitution of the double bond as in **1** and **2**. The utilization of α,β-unsaturated sulfones as dienophiles had previously been implemented,[15] but the synthetic potential of the process had not been expolited. In a relevant study, Konovalov observed that ethyl vinyl sulfone is only 50% less reactive than methyl acrylate toward cyclopentadiene and 2,3-dimethylbutadiene.[15g] Moreover, high levels of regiocontrol were anticipated from the arylsulfonyl group, although this tissue had not earlier been addressed.



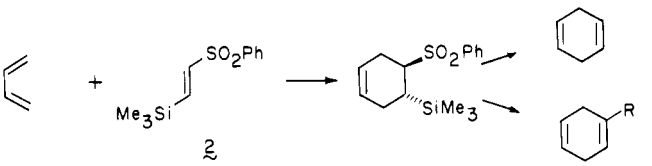
1

Where **1** is concerned, the intent was to subject the resulting adducts to reductive desulfonylation as the means of achieving ethylene equivalency. Since α-sulfonyl carbanions are readily formed, the added expectation was that alkylation prior to removal of the activating group would increase versatility and provide products formally derived from cycloadditive capture of terminal alkenes. Since **1** is also capable of metalation at C-1,[16] it is in principle possible to introduce the R group at an earlier stage in this brief sequence. However, because an added α substituent is certain to diminish the rate of cycloaddition, this approach was not given attention.

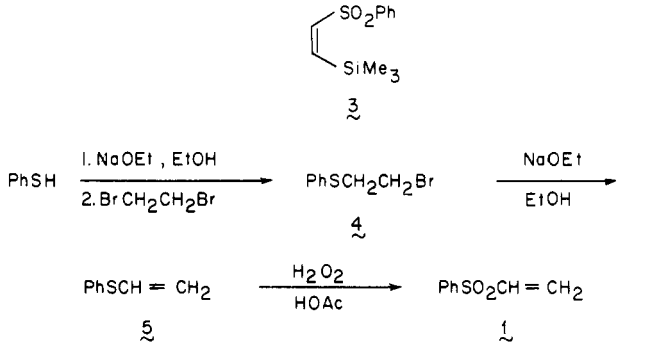
Scheme I



Although the problem of kinetic retardation is present in **2**, this disadvantage is offset by the ease with which its adducts undergo efficient fluoride-induced elimination under exceptionally mild conditions.[17,18] As will be shown, this protocol and the alkylation-mediated option have proven serviceable for the ready incorporation of HC≡CH, HC≡CD, DC≡CD, RC≡CH, and RC≡CD into six-membered rings. Unexpectedly, cis isomer **3** was observed in a limited number or experiments to be less reactive than **2**. This paper contains a complete account of our communicated studies in this area.[19]

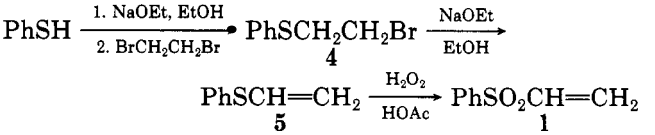


2



Synthesis of the Dienophiles

The preparation of phenyl vinyl sulfone began with the condensation of sodium thiophenoxide with 1,2-dibromoethane. The previously published method for obtaining



(5) (a) Alder, K.; Stein, G.; Finzelhagen, H. *Justus Liebigs Ann. Chem.* **1931**, *485*, 223. (b) Alder, K.; Stein, G.; Reese, J.; Grassmann, W. *Ibid.* **1932**, *496*, 204. (c) Cava, M. P.; Scheel, F. M. *J. Org. Chem.* **1967**, *32*, 1304.

(6) (a) Eaton, P. E.; Chakraborty, U. R. *J. Am. Chem. Soc.* **1978**, *100*, 3634. (b) Eaton, P. E.; Sidhu, R. S.; Langford, G. E.; Cullison, D. A.; Pietruszewski, C. L. *Tetrahedron* **1981**, *37*, 4479.

(7) Hyman, J.; Freirich, E.; Lidov, R. E. U.S. Patent 2 875 256; *Chem. Abstr.* **1959**, *53*, 12082.

(8) Dehydrobromination of vinyl bromide adducts: Sauer, J. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 211.

(9) Zinc-induced dechlorination of *cis*-1,2-dichloroethylene-derived substrates: (a) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193. (b) Cristol, S. J.; Bly, R. K. *Ibid.* **1960**, *82*, 6155. (c) Figeys, H. P.; Dralants, A. *Tetrahedron* **1972**, *28*, 2031.

(10) Thermal extrusion of cyclopentadiene from norbornadiene adducts: MacKenzie, K. *J. Chem. Soc.* **1960**, 473.

(11) Cycloaddition of 2-thioxo-1,3-dioxol-4-ene with reactive dienes [Anderson, W. K.; Dewey, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7161. Daub, J.; Erhardt, U.; Kappler, Trantz, V. *J. Organomet. Chem.* **1974**, *69*, 423] followed by treatment with trimethyl phosphite [Corey, E. J.; Winter, R. A. E. *J. Am. Chem. Soc.* **1963**, *85*, 2677], [Ni(COD)$_2$] [Semmelhack, M.; Stauffer, R. *Tetrahedron Lett.* **1973**, 2667], or Fe(CO)$_5$ [cf. Daub listing above].

(12) Diene addition to dimethyl acetylenedicarboxylate, hydrolysis, and decarboxylation, either by direct methods[9c] or involving prior chromous ion reduction: Paquette, L. A.; Wyvratt, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 4671.

(13) Formation of maleic anhydride adducts, hydrolysis, and oxidative decarboxylation by one of several techniques: Snow, R. A.; Degenhardt, C. R.; Paquette, L. A. *Tetrahedron Lett.* **1976**, 4447 and references cited therein.

(14) Phenyl vinyl sulfoxide addition and in situ thermal extrusion of phenylsulfenic acid: Paquette, L. A.; Moerck, R. E.; Harirchian, B.; Magnus, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 1597.

(15) (a) Alder, K.; Rickert, H. F.; Windenmuth, E. *Chem. Ber.* **1938**, *71*, 2451. (b) Lambert, A.; Rose, J. D. *J. Chem. Soc.* **1949**, 46. (c) Snyder, H. R.; Anderson, H. V.; Hallada, D. P. *J. Am. Chem. Soc.* **1951**, *73*, 3258. (d) Philips, J. C.; Oku, M. *Ibid.* **1972**, *94*, 1012. (e) Philips, J. C.; Oku, M. *J. Org. Chem.* **1972**, *37*, 4479. (f) Konovalov, A. I. *Dokl. Akad. Nauk SSSR* **1963**, *149*, 1334. (g) Konovalov, A. I. *Ibid.* **1965**, *162*, 343. (h) Claisse, J. A.; Davies, O. I.; Alden, C. K. *J. Chem. Soc. C* **1966**, 1498. (i) Maccagnani, G.; Montanari, F.; Taddei, F. *J. Chem. Soc. B* **1968**, 453. (j) Laping, K.; Hanack, M. *Tetrahedron Lett.* **1979**, 1309.

(16) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279.

(17) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649.

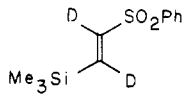
(18) For more recent applications of this elimination, see: Hsiao, C.-N.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 3455.

(19) (a) Carr, R. V. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 853. (b) Paquette, L. A.; Williams, R. V. *Tetrahedron Lett.* **1981**, *22*, 4643.

4 proceeded in low yield and afforded chiefly 1,2-bis(phenylthio)ethane.[20] While the problem of efficiency could easily be overcome by making recourse to inverse addition, the powerful alkylating properties of 4, which can cause severe skin blistering, made it desirable to avoid its handling on a large scale and to proceed directly to 5 in a one-pot procedure. The conversion to phenyl vinyl sulfide which is detailed herein proceeds in 88% overall yield.[21] Oxidation of 5 by the Bordwell–Pitt procedure[22] gave 1.

To arrive at 2, we condensed trimethylvinylsilane with benzenesulfonyl chloride in the presence of cuprous chloride, and the free-radical addition product (6, Scheme I) was dehydrochlorinated with triethylamine in the manner outlined previously by Calas and co-workers.[23] Alternatively, we have found that 2 and its cis isomer 3 can be individually prepared in acceptable yield from the readily available[24] common acetylenic precursor 7 by hydrogenation at 50 psi in ethyl acetate solution. In the absence of pyridine, 3 experiences efficient catalyzed isomerization to the *E* isomer.

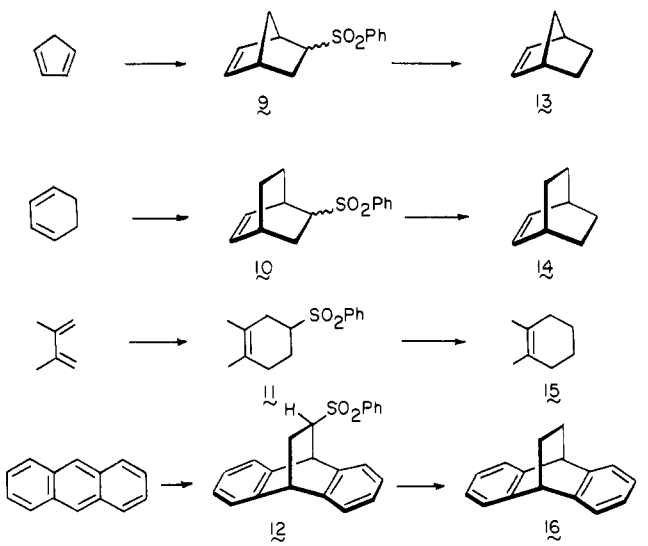
The latter scheme lends itself to the convenient preparation of isotopically labeled 8 merely by substituting a deuterium atmosphere under otherwise identical conditions.



8

Cycloaddition Behavior of 1

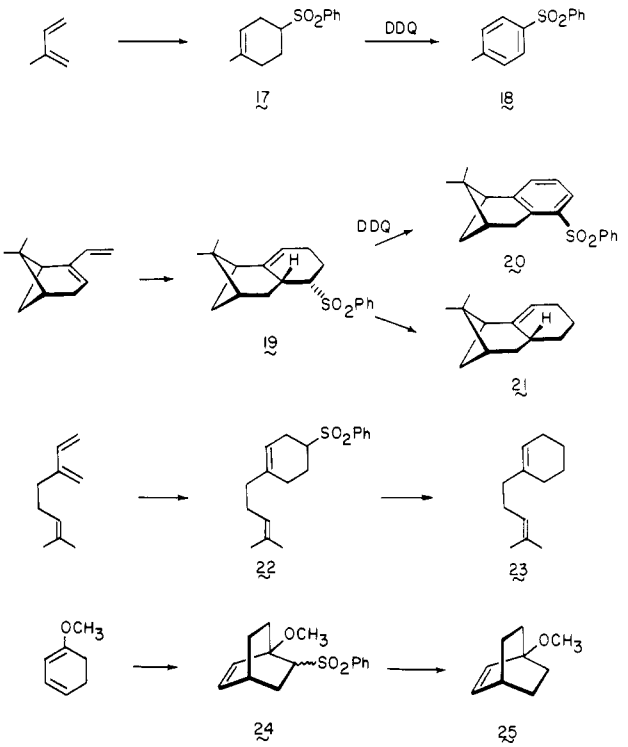
In order to gauge the dienophilic reactivity of 1, cyclopentadiene, 1,3-cyclohexadiene, 2,3-dimethylbutadiene, and anthracene were admixed with the vinyl sulfone in a small amount of benzene, in a sealed tube if necessary.



Cycloaddition to cyclopentadiene was observed to proceed slowly at 25 °C. After 40 h, 9 was produced quantitatively as a 22:78 exo/endo mixture of isomers.[15i] With the less reactive dienes, more forcing conditions were required (125 °C, 17 h; 135 °C, 32 h; 155 °C, 100 h, respectively). All three reactions proceeded smoothly to provide 10 (19:81 exo/endo, 89%), 11 (94%), and 12 (96%) as colorless crystalline solids. Several attempts to induce Lewis acid catalysis in these examples gave no evidence of rate acceleration; some darkening and product destruction occurred instead.

Reductive desulfonylation of 9–12 was most efficiently accomplished with excess 6% sodium amalgam in disodium hydrogen phosphate buffered methanol at −20 °C.[25] The yields of hydrocarbons 13–16 ranged from 76% to 94%. The lower efficiencies were noted for the more volatile substances and likely reflect mechanical losses incurred during their isolation rather than complications intrinsic to the method.

To assess the question of regiochemistry, 1 was treated with isoprene, nopadiene, myrcene, and 2,3-dihydroanisole at elevated temperatures. Direct chromatographic and spectral analysis of the unpurified adducts (17, 19, 22, 24)



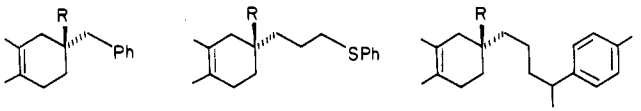
showed that a single isomer had been produced efficiently in each instance. Dehydrogenation of 17 with DDQ gave the known phenyl *p*-tolyl sulfone (18) and confirmed the para orientation of the key substituents. Identical treatment of 19 afforded 20. Since the phenylsulfonyl group exerts only low level shielding effects on proximate aryl protons, much like a halogen atom, the three-proton aromatic pattern in 20 (after discounting those resonances due to the phenyl ring) expectedly compares very closely to that of 3-bromo-*o*-xylene[26a] and differs substantially from that of 4-bromo-*o*-xylene.[26b] The remainder of the spectrum is quite similar to that of benzopinane.[27] The structural assignments to 22 and 24 [an 18% exo/82% endo (syn to double bond) mixture], which were advanced

(20) Claisse, J. A.; Davies, D. I.; Alden, C. K. *J. Chem. Soc. C* **1966**, 1498.
(21) Paquette, L. A.; Carr, R. V. C. *Org. Synth.*, in press.
(22) Bordwell, F. G.; Pitt, B. M. *J. Am. Chem. Soc.* **1955**, *77*, 572.
(23) Pillot, J.-P.; Dunogues, J.; Calas, R. *Synthesis* **1977**, 469.
(24) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970**, *1*, 145.
(25) Trost, B. M.; Arndt, H. C.; Strege, P. E.; Verhoeven, T. R. *Tetrahedron Lett.* **1976**, 3857.
(26) (a) "Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974; Vol. 4, No. 59A. (b) Ibid. Vol. 4, No. 60B.
(27) Paquette, L. A.; Melega, W. P.; Kramer, J. D. *Tetrahedron Lett.* **1976**, 4033.

on the basis of the prior findings, conform fully to the observed spectral properties. The efficiency with which conversion to hydrocarbons **21** and **23** and to ether **25** could be achieved (91–97% yields) is particularly noteworthy.

Alkylation–Desulfonylation of the Adducts

At this juncture, our attention became focused upon achieving alkylative desulfonylation of selected adducts. By condensation of the derived α-sulfonyl carbanions with electrophiles, site-specific functionalization could be readily achieved. Subsequent removal of the phenyl sulfonyl residue provided for fully regiocontrolled incorporation of widely varied side chains onto a cyclohexene ring in quite acceptable yield. A particular advantage of the method is the stability of numerous functional groups, e.g., SPh, $Si(CH_3)_3$, $COOC_2H_5$, etc., to the action of sodium amalgam. As can be seen from the examples which follow, a rich selection of terminal olefinic synthons is made available in this fashion. Initial studies were carried out with sulfone **11**. Generation of the anion with *n*-butyllithium in anhydrous tetrahydrofuran at −60 °C was followed by dropwise addition of the individual bromides. Products **26a**, **27a**, **28a** were isolated in yields of 86%, 86%, and

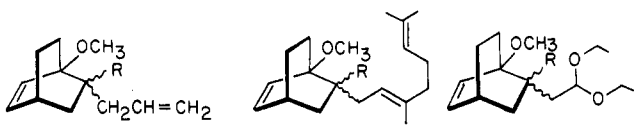


26 **27** **28**

a, R = SO_2Ph ; **b**, R = H

81%, and their subsequent desulfonylation proved equally efficient (83–96%). The formation of **26b** is notable since the overall reaction sequence constitutes formal capture of allylbenzene in a [4 + 2] cycloaddition. Attempts to achieve this result directly would likely cause prototropic shift and/or polymerization in the unactivated dienophile.

The reactivity of **24** proved entirely comparable and led via **29a–31a** (83–95%) to ethers **29b–31b** (80–95%). In

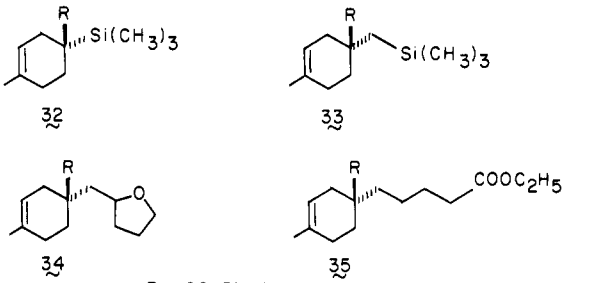


29 **30** **31**

a, R = SO_2Ph ; **b**, R = H

the first two examples, the alkylations were carried out in 90% tetrahydrofuran–10% hexamethylphosphoramide (HMPA) solution in an effort to enhance the levels of product formation. Once again, no troublesome side reactions were encountered. The isolation of **29b** and **30b** provides dramatic illustration of the fact that synthons for 1,4-pentadienes can be easily incorporated with excellent regiocontrol.

Another useful feature of this methodology is the readiness with which vinylsilane and allylsilane synthons can be regiospecifically incorporated. Electronic factors within these substrates, and their congeners as well, are insufficiently dominant to guarantee useful regiochemical control. In the event, trapping of the anion of **17** with chlorotrimethylsilane and trimethylsilylmethyl triflate followed by desulfonylation served to deliver **32b** and **33b** in very acceptable overall yields. Two additional examples are provided by **34** and **35**. In the last instance, reduction was conducted at room temperature in ethanol–tetrahydrofuran (4:1) to preclude ester interchange.



32 **33** **34** **35**

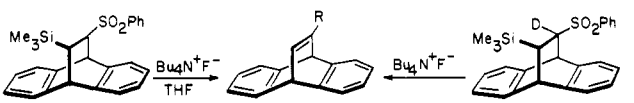
a, R = SO_2Ph ; **b**, R = H

Cycloaddition Behavior of 2

The lesser dienophilic reactivity of **2** relative to **1** became immediately apparent upon reaction with cyclopentadiene at 20 °C. Only after 3.5 days was the cycloaddition judged to be complete (TLC analysis). Under these conditions, there was produced a separable 2:1 mixture of **36** and **37** in 89% yield. These isomers were readily identified by the chemical shift and multiplicity of their respective α-sulfonyl protons (δ 3.47, dd, J = 6, 3 Hz; δ 2.76, d, J = 6 Hz). The observed product ratio, which is not too dissimilar from that found in **9**, indicates that the phenylsulfonyl group exhibits a greater tendency for secondary orbital overlap than trimethylsilyl, as expected. More interesting was the subsequent finding that **3** adds to cyclopentadiene in hot benzene to give **38** (58%) where both substituents are endo oriented. At ambient temperature, the still less reactive **3** required 2.5 weeks to be transformed into **38** (30% yield).

Although **36–38** could individually be transformed into norbornadiene by heating with anhydrous tetra-*n*-butylammonium fluoride in tetrahydrofuran, the volatility of the hydrocarbon product made isolation difficult and inefficient. For this reason, these adducts were converted to **39–41** (Scheme II) by reaction with 1,3-diphenylisobenzofuran. Subsequent olefination of these polycyclic systems under analogous conditions led efficiently (>85%) to bridged ether **42**[5c] in each instance. Thus, no geometric restrictions to introduction of the double bond are apparent. However, this is not to say that there is no stereochemical dependence, since prior equilibration of the phenylsulfonyl substituent in the presence of fluoride ion remains a possibility. However, this point is discounted by certain observations which follow.

Anthracene was smoothly and efficiently (98%) transformed into **43** when heated with **2** in toluene solution at 160 °C in a sealed tube for 7 days. As before, cis isomer **3** proved less satisfactory for our purposes, condensation with anthracene for 2 weeks affording only low yields (35%) of **43**. No cis product was found over the entire course of reaction. The reactivity or **43** toward tetra-*n*-butylammonium fluoride appears to be somewhat higher than that of **36–38**, conversion to dibenzobarrelene (**45a**, 84%) being complete within 1 h.

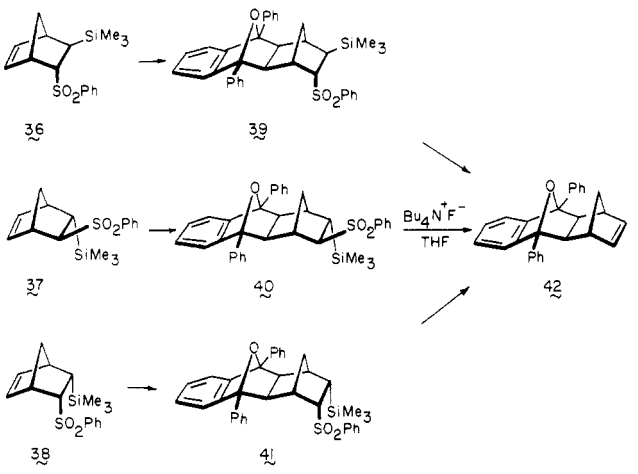


43 **45a**, R = H; **b**, R = D **44**

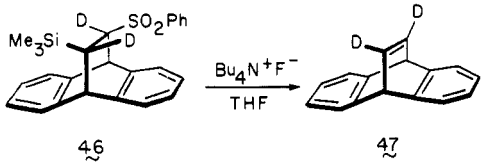
Sequential treatment of **43** with *n*-butyllithium and water (both normal and inverse quenching) returned only the trans isomer. Substitution of D_2O for water led to **44** and subsequently **45b**.

Adaptation of the same conditions to **8** furnished the isotopically labeled silyl sulfone **46**. The ensuing fluoride ion promoted elimination proceeded without measurable

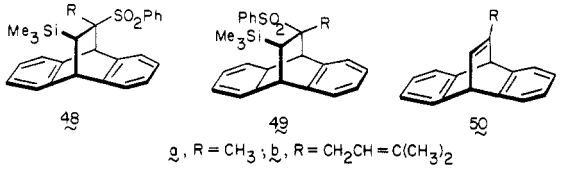
Scheme II



washout of deuterium α to the sulfonyl substituent and delivered **47**.



Attention is called to the fact that the deuteration of **43** proceeded most satisfactorily when 2.5–3 equiv of *n*-butyllithium was employed. The same stoichiometry was required to attain maximized yields of alkylation products. With methyl iodide, a mixture of **48a** and **49a** resulted.



g, R = CH_3; **h**, R = $CH_2CH{=}C(CH_3)_2$

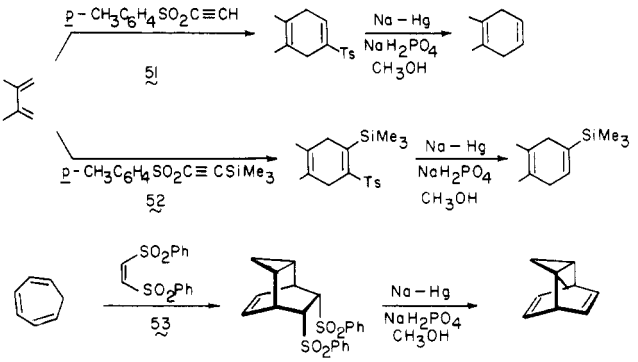
Although these epimers could be separated and individually converted to **50a**, it was not possible to assign their relative stereochemistries by spectral means alone. A similar profile was noted when the α-sulfonyl carbanion was captured by prenyl bromide. Clearly, steric control gains importance in those reactions where sterically more demanding reagents become involved.

The equally facile formation of **50a** and **50b** from epimeric silyl sulfones **48** and **49**, molecules which are not capable of base-promoted epimerization, is noteworthy. Since a trans-antiplanar arrangement of groups is not mandatory, it would appear that the α-sulfonyl carbanion is capable of configurational inversion under the reaction conditions employed here.

Discussion and Recent Developments

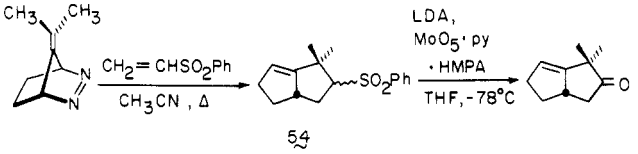
Vinyl sulfones **1** and **2** are readily prepared reagents which can serve as useful ethylene, acetylene, 1-alkene, and 1-alkyne equivalents in Diels–Alder reactions. Although the average reactivity of these dienophiles may make them unsuitable for certain applications, successful adduct formation provides substances which can be efficiently desulfonylated or smoothly eliminated. The relatively mild conditions of these follow-up steps are tolerant to a wide range of functional groups.[28,29]

Scheme III



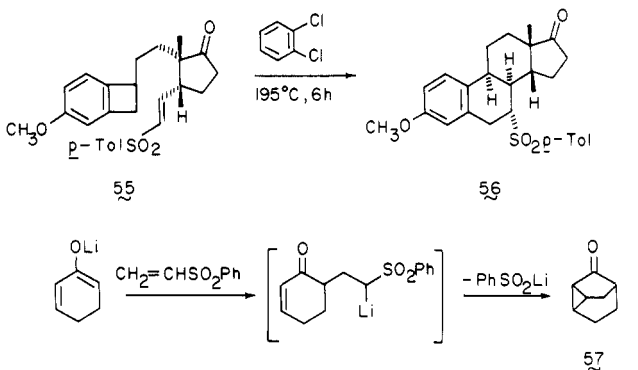
During the course of this investigation, Davis and Whitham reported that ethynyl *p*-tolyl sulfone (**51**) and *p*-tolyl 2-(trimethylsilyl)ethynyl sulfone (**52**) can be utilized as acetylene equivalents in Diels–Alder reactions[30] (Scheme III). Analogously, DeLucchi and Modena developed *cis*-1,2-bis(phenylsulfonyl)ethylene (**53**) into an acetylene synthon.[31]

As shown by Little, **1** is also an excellent trap for 1,3-diyls.[32] Furthermore, the anions of the resulting adducts (e.g., **54**) experience efficient oxidative desulfonylation to



form ketones upon treatment with MoOPh in tetrahydrofuran solution at −78 °C.[33] Thus, **1** can equally well be deployed as a ketene equivalent in [4 + 2] cycloadditions.

An extension of the previously discussed concepts to the intramolecular reaction of **55** → **56** has now appeared.[34] The versatility of phenyl vinyl sulfone (**1**) had been expanded still more by the observation that its involvement in the bicycloannulation of cyclohexenone anions delivers tricyclo[3.2.0.$0^{2,7}$]octan-6-ones such as **57** in variable yields.[35]



Finally, a group of useful conjugate addition reactions of **1** and related vinyl sulfones which show synthetic promise has recently been uncovered. This new methodology includes six-membered-ring annulation,[36,37] ste-

(28) For a more recent example, consult: Daniels, R. G.; Paquette, L. A. *J. Org. Chem.* **1981**, *46*, 2901.
(29) See also: Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 4566.
(30) Davis, A. P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1980**, 639.
(31) DeLucchi, O.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1982**, 914.
(32) Little, R. D.; Brown, L. *Tetrahedron Lett.* **1980**, *21*, 2203.
(33) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, *21*, 3339.
(34) Kametani, T.; Aizawa, M.; Nemoto, H. *Tetrahedron* **1981**, *37*, 2547.
(35) Cory, R. M.; Renneboog, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1081.

reoselective cuprate additions,[38] and condensation reactions with α-metalated nitriles.[39] Ban and co-workers have nicely demonstrated that phenyl 2-(trimethylsilyl)ethyl sulfone can serve as a masked vinyl cation.[40]

Experimental Section

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian EM-390, Varian T-60, Bruker WP-200, and Bruker WM-300 spectrometers. Carbon spectra were recorded with a Bruker WP-80 instrument. Mass spectra were determined on AEI-MS9 and Kratos MS25 spectrometers at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Phenyl Vinyl Sulfide (5). To an ethanolic sodium ethoxide solution [prepared from 23 g (1 mol) of sodium metal and 400 mL of absolute ethanol] was added benzenethiol (110 g, 1 mol) during 15–20 min. The resulting solution was maintained under nitrogen while transferred during 45 min to a stirred solution of 1,2-dibromoethane (272 g, 1.45 mol) in ethanol (18 mL). This mixture was stirred under nitrogen for 30 min, at which point an additional 1 mol of ethanolic sodium ethoxide solution (prepared as above) was introduced during 30 min. The stirred reaction mixture was heated at the reflux temperature for 8 h, cooled, and treated with benzene (500 mL) and water (500 mL). The organic layer was separated, washed with water (2 × 500 mL) and brine (100 mL), and concentrated. The yellow oil so isolated was distilled to give 120 g (88%) of **5** as a colorless oil: bp 91–93 °C (20 torr); IR (neat) 3040, 1585, 1475, 1435, 1085, 1020, 950, 735, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.32 (m, 5 H), 6.50 (dd, J = 18, 12 Hz, 1 H), 5.25 (two superimposed d, J = 18, 12 Hz, 2 H).

Phenyl Vinyl Sulfone (1). Hydrogen peroxide (30%, 56 mL, 0.5 mol) was added slowly to a magnetically stirred solution of **5** (19.7 g, 0.145 mol) in glacial acetic acid (70 mL) at such a rate as to maintain a reaction temperature of 70 °C. The reaction mixture was heated at the reflux temperature for 20 min, cooled, and treated with ether (150 mL) and water (200 mL). The organic phase was separated, washed with water and brine, and heated at 70 °C and 0.3 torr for 3 h. There was obtained 19.0 g (78%) of **1** as a colorless solid: mp 66–67 °C (from hexane); IR ($CHCl_3$) 3020, 1445, 1380, 1315, 1145, 1080, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (m, 2 H), 7.55 (m, 3 H), 6.75 (dd, J = 17, 10 Hz, 1 H), 6.33 (d, J = 17 Hz, 1 H), 5.96 (d, J = 10 Hz, 1 H).

***trans*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethylene (2). (A) From Trimethylvinylsilane.**[23] Trimethylvinylsilane (10 g, 0.1 mol), benzenesulfonyl chloride (17.65 g, 0.1 mol), cuprous chloride (0.1 g), and triethylamine hydrochloride (0.2 g) in dichloromethane (10 mL) and acetonitrile (2 mL) were sealed in a Carius tube under vacuum. The tube was placed in a steel autoclave containing dichloromethane, heated to 130 °C for 10 h, cooled to −78 °C, and opened. The mixture was poured into dilute hydrochloric acid (150 mL), and the organic phase was washed with dilute hydrochloric acid (150 mL) and disodium EDTA solution (2 × 150 mL). Following drying the solvent evaporation, there was obtained 21.57 g (78%) of **6**, essentially pure by ^1H NMR.

The unpurified chloride (21.57 g, 0.078 mol) and triethylamine (50 mL) in benzene (300 mL) were stirred at ambient temperature for 48 h and poured into dilute hydrochloric acid (250 mL). The separated organic phase was washed with dilute hydrochloric acid (100 mL), saturated sodium bicarbonate solution (250 mL), and water (250 mL) prior to drying and solvent evaporation. There was obtained 18.15 g (97%) of **2** as a colorless oil which was crystallized by dissolution in the minimal amount of hot methanol and cooling to −20 °C; mp 60 °C (lit.[23] mp 60 °C).

(B) Catalytic Hydrogenation of 7. A solution of **7** (0.40 g, 1.7 mmol) in ethyl acetate (100 mL) was hydrogenated at 50 psi over 5% palladium on carbon (0.25 g) for 4.5 h. After filtration, evaporation of the filtrate, and chromatography, there was obtained 0.195 g (48%) of **2**, identical in all respects with the material prepared in part A.

***cis*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethylene (3).** A solution of **7** (5.0 g, 0.021 mol) in ethyl acetate (100 mL) and pyridine (10 mL) was hydrogenated over 5% Pd/C as described above. Following product isolation, pure **3** was obtained by chromatography on silica gel (elution with petroleum ether–ethyl acetate, 95:5); 1.76 g (35%) of clear colorless oil. The spectral properties of **3** were identical with those previously reported.[23]

***(E)*-1,2-Dideuterio-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene (8).** A solution of **7** (1.0 g, 4.2 mmol) in ethyl acetate (20 mL) containing 250 mg of 5% Pd/C was placed in a 50 mL filter flask equipped with a stopcock and connected to a lecture bottle of deuterium via a side arm. The flask was evacuated and then filled with deuterium to 36 psi. The mixture was stirred at ambient temperature for 36 h, filtered, and evaporated. The residue was subjected to silica gel chromatography (elution with petroleum ether–ethyl acetate, 95:5) to give **8** as colorless plates, identical with **2** except for the absence of olefinic protons in the ^1H NMR spectrum.

Cycloaddition of 1 to Cyclopentadiene. A solution of freshly distilled cyclopentadiene (3.0 g, 45 mmol) and **1** (1.90 g, 11.3 mmol) in benzene (15 mL) was placed in a stoppered flask and allowed to stand for 40 h. The solvent was evaporated, and *endo*-dicyclopentadiene was removed at 50 °C and 0.3 torr. The oily residue was chromatographed on silica gel (45 g, elution with 15% ethyl acetate in hexane). The early fractions contained 210 mg of pure *exo*-**9**: white crystalline solid; mp 65–66 °C (lit.[15i] mp 66–67 °C); IR (CCl_4) 3058, 2978, 2940, 1438, 1310, 1145, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (m, 2 H), 7.53 (m, 3 H), 6.18 (m, 2 H), 3.20 (m, 1 H), 3.01 (m, 1 H), 2.86 (m, 1 H) 2.30–1.77 (m, 2 H), 1.57–1.18 (m, 2 H); MS, m/e (M^+) calcd 234.0714, obsd 234.0720.

Continued elution gave a fraction (1.13 g) containing a 65:35 mixture (^1H NMR integration) of *endo*- and *exo*-**9**. Finally, 850 mg of *endo*-**9** was isolated as a white crystalline solid: mp 67.5–69 °C (lit.[15i] mp 65–65 °C); IR (CCl_4) 3060, 2965, 2930, 2858, 1445, 1312, 1148, 717, 686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (m, 2 H), 7.52 (m, 3 H), 6.17 (m, 2 H), 3.57 (ddd, J = 8.5, 5.3, 3.5 Hz, 1 H), 3.00 (m, 2 H), 2.03 (dd, J = 12.5, 3.5 Hz, 1 H), 1.65–1.33 (m, 3 H); MS, m/e (M^+) calcd 234.0714, obsd 234.0720.

The overall yield of **9** was quantitative with an exo/endo ratio of 22:78.

Reductive Desulfonylation of 9. General Procedure. A 1.0-g (4.54 mmol) sample of **9** (isomer mixture) dissolved in anhydrous tetrahydrofuran (4 mL) was added to a mixture of 6% sodium amalgam (9.3 g, 18.6 mol of Na) and disodium hydrogen phosphate (3.0 g, 21.1 mmol) in methanol (20 mL, distilled from calcium hydride or magnesium methoxide) under argon. The reaction mixture was stirred for 11 h at which point TLC analysis indicated the total consumption of **9**. The contents of the flask were decanted into a separatory funnel. The flask was rinsed with pentane (2 × 40 mL), and the total organic solution was washed with water (4 × 25 mL) and brine (25 mL) prior to drying and careful solvent removal. Molecular distillation of the residue gave 340 mg (80%) of norbornene, the spectra of which were identical with those of an authentic sample.[41]

5-(Phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (10). A small Carius tube was charged with 1,3-cyclohexadiene (800 mg, 10 mmol), **1** (610 mg, 3.63 mmol), benzene (2 mL), and a few crystals of hydroquinone. The tube was flushed with argon, sealed under vacuum, and heated to 123–125 °C for 17 h. The reaction mixture was directly chromatographed on silica gel (45 g). Elution with hexane removed nonpolar material, while elution with 15% ethyl acetate in hexane afforded 810 mg (90%) of **10** as a 4:1 endo/exo mixture. A fraction containing the pure endo isomer was used for characterization: IR (neat) 3070, 3010, 2945, 1460, 1355, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.77–7.23 (m, 5 H), 6.21–5.96 (m, 2 H),

(36) Pouton, J.; Helquist, P.; Conrad, P. C.; Fuchs, P. L. *J. Org. Chem.* **1981**, *46*, 118.
(37) Fabrissin, S.; Fatutta, S.; Risaliti, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 109.
(38) DeChirico, G.; Fiandanese, V.; Marchese, G.; Naso, F.; Sciacovelli, O. *J. Chem. Soc., Chem. Commun.* **1981**, 523.
(39) Agawa, T.; Yoshida, Y.; Komatsu, M.; Ohshiro, Y. *J. Chem. Soc., Perkin Trans. 1* **1981**, 751.
(40) Ohmuna, T.; Hata, N.; Fujiwara, H.; Ban, Y. *J. Org. Chem.* **1982**, *47*, 4713.
(41) "Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, 1974, Vol. 1, No. 45B.

3.28 (ddd, J = 8.0, 6.5, <1 Hz, 1 H), 2.93 (m, 1 H), 2.58 (m, 1 H), 1.95–1.06 (m, 6 H); MS, m/e (M^+) calcd 248.0871, obsd 248.0877.

Reductive Desulfonylation of 10. A 505-mg (2.04 mmol) sample of 10 (mixture of isomers) was reduced in the predescribed nanner for 3.5 h. The pentane solution was carefully concentrated through a short Vigreux column and filtered through 2 g of basic alumina to give bicyclo[2.2.2]octene (173 mg, 78.5%) as a colorless mobile liquid: ^{1}H NMR ($CDCl_3$) δ 6.19 (sextet, 2 H), 2.51 (m, 2 H), 1.77–1.21 (m, 8 H); ^{13}C NMR ($CDCl_3$) 134.4, 29.6, 25.9 ppm.

1,2-Dimethyl-4-(phenylsulfonyl)cyclohexene (11). A mixture of 2,3-dimethylbutadiene (11.4 g, 13.9 mmol),[42] 1 (22.0 g, 13.1 mmol), benzene (20 mL), and hydroquinone (50 mg) was heated in an evacuated Carius tube at 135 °C for 22 h. The crude product was chromatographed on silica gel (170 g) to give 30.7 g (93.7%) of 11 as a colorless crystalline solid: mp 79.5–81 °C; IR (CCl_4) 3060, 3010, 2955, 2920, 1445, 1320, 1145, 715, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.62–7.37 (m, 5 H), 3.07 (m, 1 H), 2.31–1.30 (series of m, 6 H), 1.60 (br s, 6 H); MS, m/e (M^+) calcd 250.1027, obsd 250.1033. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 67.28; H, 7.26.

1,2-Dimethylcyclohexene (15). The general desulfonylation procedure (pentane workup) was applied to 970 mg (3.9 mmol) of 11. After 5.5 h and distillative removal of the pentane, the residue was molecularly distilled to furnish 320 mg (76%) of **15** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.04–0.87 (series of m, 8 H), 1.61 (s, 6 H); ^{13}C NMR ($CDCl_3$) 125.5, 31.9, 23.6, 19.2 ppm (lit.[43] 125.6, 31.9, 23.7, 19.2).

Cycloaddition of 1 to Anthracene. A mixture of anthracene (1.30 g, 7.3 mmol), phenyl vinyl sulfone (1.0 g, 5.95 mmol), and benzene (7 mL) was heated in an evacuated Carius tube at 155 °C for 100 h and worked up as described above. The residue was taken up in chloroform (30 mL) and filtered to remove 120 mg of anthracene. The filtrate was concentrated to ca. 5 mL and chromatographed on silica gel (50 g). Elution with pentane–chloroform (1:1) gave an additional 170 mg of anthracene. Further elution with chloroform yielded **12** (1.97 g, 96%) as a white crystalline solid: mp 138–141 °C (from chloroform–hexane, 1:3); IR (CCl_4) 3064, 3020, 2945, 1460, 1448, 1322, 1100, 908, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.61–6.73 (m, 13 H), 4.68 (d, J = 2.2 Hz, 1 H), 4.20 (dd, J = 3.0, 2.5 Hz, 1 H), 3.28 (ddd, J = 9.0, 6.5, 2.2 Hz, 1 H), 2.12–1.83 (m, 2 H); MS, m/e (M^+) calcd 346.1027, obsd 346.1035.

Dibenzobicyclo[2.2.2]octadiene (16). Reductive desulfonylation of 198 mg (0.57 mmol) of **12** as before (benzene workup) gave a crude product which was filtered through alumina (5 g, benzene elution). There was isolated 110 mg (94%) of **16** as colorless crystals: mp 139–141 °C (lit.[9a] mp 142–143 °C); ^{1}H NMR ($CDCl_3$) δ 7.01 (m, 8 H), 4.13 (m, 2 H), 1.68 (m, 4 H), identical with a previous literature report;[44] ^{13}C NMR ($CDCl_3$) 143.8, 125.5, 123.2, 44.1, 26.7 ppm (compare lit.[45]).

1-Methyl-4-(phenylsulfonyl)cyclohexene (17). A mixture of isoprene (10.1 g, 0.148 mol), 1 (18.2 g, 0.108 mol), benzene (15 mL), and hydroquinone (27 mg) was heated at 120 °C in a sealed Carius tube for 28 h. The crude isolated product was eluted through silica gel (70 g) with 20% ethyl acetate in hexane, and 23.7 g (93%) of **17** was recovered as a colorless, crystalline solid: mp 79–81 °C; IR (CCl_4) 3060, 3010, 2960, 2925, 2900, 148, 1320, 1148, 720, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.82 (m, 2 H), 7.55 (m, 3 H), 5.27 (m, 1 H), 3.05 (m, 1 H), 2.35–1.33 (series of m, 6 H), 1.59 (br s, 3 H); ^{13}C NMR ($CDCl_3$) 137.5, 134.0, 133.6, 129.1, 128.9, 117.7, 60.1, 29.2, 24.8, 23.0, 22.1 ppm. Anal. Calcd for $C_{13}H_{16}O_2S$: C, 67.17; H, 7.25. Found: C, 67.28; H, 7.26.

Dehydrogenation of 17. Into a small Carius tube were placed 490 mg (2.08 mmol) of **17**, 1.10 g (4.85 mmol) of DDQ, and 7.5 mL of benzene. The tube was flushed with argon, sealed in vacuo, and heated at 155 °C for 32 h. The dark reaction mixture was taken up in benzene (45 mL), extracted with 10% sodium carbonate solution (2 × 50 mL), and washed with water prior to drying. The light red solution was concentrated and the residue subjected to preparative TLC on silica gel (elution with 40% ethyl acetate in hexane). The fifth and largest band was collected to give 189 mg of a beige solid, approximately 60% pure by ^{1}H NMR analysis. This material was re-submitted to preparative TLC with little improvement in purity. However, threefold recrystallization from hexane-ether (4:1) afforded pure **18** as colorless flakes, mp 123–125 °C (24 mg, 5.0%) (lit. mp 126 °C,[46] 125–125.5 °C[47]). The ^{1}H NMR spectrum was identical to that reported.[48]

Cycloaddition of 1 to Nopadiene. A mixture of nopadiene[27] (2.60 g, 17.6 mmol), 1 (2.0 g, 11.9 mmol), benzene (4 mL), and hydroquinone (0.05 g) was heated in an evacuated Carius tube at 150 °C for 28 h. After the workup, the residue was chromatographed on silica gel (35 g, elution with 20% ethyl acetate in hexane) to afford 3.70 g (98%) of **19** as a colorless viscous oil: IR (neat) 3020, 2965, 2920, 1452, 1385, 1368, 1320, 1148 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.93–7.65 (m, 2 H), 7.63–7.40 (m, 3 H), 5.20 (m, 1 H), 2.98 (m, 1 H), 1.25 (s, 3 H), 0.97 (s, 3 H), 2.7–0.73 (series of m, 11 H); MS, m/e (M^+) calcd 316.1497, obsd 316.1502.

Dehydrogenation of 19. An evacuated Carius tube containing 940 mg (2.97 mmol) of **19**, 1.43 g (6.30 mmol) of DDQ, and 12 mL of benzene was heated at 165 °C for 28 h. The contents were poured into a separatory funnel, and the tube was rinsed with benzene (8 × 10 mL). The combined organic layers were washed with 20% potassium carbonate solution (3 × 75 mL) and water (100 mL) prior to drying and solvent evaporation. The residual brown oil (1.07 g) was subjected to preparative TLC on silica gel (elution with 30% ethyl acetate in hexane). The third band (480 mg) was rechromatographed to give **20** as a colorless semisolid which was not further purified: ^{1}H NMR ($CDCl_3$) δ 8.1–6.75 (series of m, 8 H), 3.1–1.0 (series of m, 6 H), 1.02 (s, 3 H), 0.98 (s, 3 H) (see text for additional comments).

Reductive Desulfonylation of 19. Treatment of **19** (650 mg, 2.06 mmol) in tetrahydrofuran solution (4 mL) with 6% sodium amalgam (4.1 g, 10.7 mol) and disodium hydrogen phosphate (1.0 g, 7.0 mmol) in dry methanol (12 mL) for 5 h and a pentane workup provided crude **21**. Elution of this material through silica gel (10 g) with pentane gave 353 mg (97%) of pure **21** as a colorless liquid: IR (CCl_4) 3020, 2980, 2920, 2860, 2825, 1666, 1452, 1385, 1368 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.03 (m, 1 H), 2.64–2.20 (m, 4 H), 1.26 (s, 3 H), 0.98 (s, 3 H), 2.18–0.75 (series of m, 9 H); MS, m/e (M^+) calcd 176.1565, obsd 176.1570.

An analytical sample was prepared by molecular distillation at 118–123 °C and 15 torr. Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.58; H, 11.45.

Cycloaddition of 1 to Myrcene. Heating a mixture of 1 (1.75 g, 10.4 mmol), myrcene (2.0 g, 14.7 mmol), benzene (3 mL), and hydroquinone (0.05 g) in an evacuated Carius tube at 155 °C for 22 h, followed by chromatography of the isolated crude product on silica gel (40 g, elution with 10% ethyl acetate in hexane), yielded 2.8 g (88.6%) of **22** as a colorless viscous liquid: IR (neat) 3060, 2960, 2905, 2840, 1673, 1587, 1440, 1305, 1145; ^{1}H NMR ($CDCl_3$) δ 7.82 (m, 2 H), 7.48 (m, 3 H), 5.28 (m, 1 H), 4.98–4.60 (m, 1 H), 3.28–2.77 (m, 1 H), 2.45–1.40 (series of m, 10 H), 1.70 (s, 3 H), 1.61 (s, 3 H); MS, m/e (M^+) 304, too weak to mass measure.

Continued elution afforded 0.20 g of unreacted 1. Accordingly, the yield of **22** based upon recovered starting material is 98%.

1-(4-Methyl-3-pentenyl)cyclohexene (23). Reductive desulfonylation of **22** (510 mg, 1.68 mmol) in the predescribed manner (pentane workup) afforded a crude product which was eluted in pentane solution through basic alumina. There was isolated 253 mg (92%) of **23** as a colorless, pleasant smelling oil: IR (neat) 2958, 2925, 2845, 2836, 1438 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.35 (m, 1 H), 5.02 (m, 1 H), 2.18–1.22 (series of m, 12 H), 1.63 (br s, 3 H), 1.58 (br s, 3 H); ^{13}C NMR ($CDCl_3$) 135.3, 131.6, 124.5, 120.8, 38.1, 28.4, 26.6, 25.6, 25.3, 23.1, 22.7, 17.6 ppm; MS, m/e (M^+) calcd 164.1565, obsd 164.1568.

An analytical sample was prepared by VPC (5 ft × 0.25 in. 15% SE-30) at 140 °C. Anal. Calcd for $C_{12}H_{20}O$: C, 87.73; H, 12.27. Found: C, 87.43; H, 12.13.

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1-Methoxy-6-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (24). Heating a mixture of 1 (5.40 g, 32.1 mmol), 2,3-dihydroanisole (7.1 g, 64.5 mmol),[49] benzene (15 mL), and hydroquinone (0.05 g) in an evacuated Carius tube at 135 °C for 18 h afforded a crude product which was chromatographed on silica gel (85 g). Elution with 25% ethyl acetate in hexane gave 6.1 g (68%) of **24** as an exo/endo (18:82) mixture of isomers. Recrystallization afforded the pure endo isomer as a colorless, crystalline solid, mp 86–88.5 °C; IR (CCl_4) 3050, 2930, 2858, 2820, 1320, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80 (m, 2 H), 7.50 (m, 3 H), 6.13 (br d, 1 H), 6.10 (s, 1 H), 3.63 (dd, J = 8.3, 7.0 Hz, 1 H), 3.13 (s, 3 H), 2.63 (m, 1 H), 2.03–1.40 (m, 6 H); MS, m/e (M^+) calcd 278.0977, obsd 278.0983. Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.73; H, 6.52. Found: C, 64.79; H, 6.63.

1-Methoxybicyclo[2.2.2]oct-2-ene (25). Reductive desulfonylation of *endo*-**24** (200 mg, 0.72 mmol) as previously described provided 90 mg (91%) of **25** as a colorless liquid after silica gel (10 g) chromatography (elution with 10% ethyl acetate in hexane): IR (CCl_4) 3035, 2925, 2802, 1451, 1110, 588 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.34–6.21 (m, 2 H), 3.34 (s, 3 H), 2.45 (br m, 1 H), 1.90–1.21 (series of m, 8 H). These spectral data are identical with those earlier reported.[50]

General Alkylation Procedure. Into a flame-dried, two-necked, round-bottomed flask was placed the appropriate sulfone under argon. Anhydrous tetrahydrofuran (5 mL/mmol of sulfone) was added via syringe, and the contents were cooled to −60 °C. The magnetically stirred solution was treated with 1.1 equiv of *n*-butyllithium in hexane via syringe and stirred in the cold for 10 min. At this point, dry HMPA (10% of the THF volume) was added if desired. The alkylating agent was introduced dropwise via syringe, and the reaction mixture was allowed to warm to room temperature during 45 min. After an additional 1–2 h of stirring, the product was poured into a saturated ammonium chloride solution and thoroughly shaken. Ether (50 mL) was added, and the aqueous layer was withdrawn. The organic phase was washed with water (2 × 25 mL) and brine, dried, and evaporated. If HMPA was used, a washing with 1 N sodium hydroxide immediately preceded the water wash. The crude products were then purified as described below.

In two instances, use was made of an inverse addition procedure. These details are provided where relevant.

1,2-Dimethyl-4-benzyl-4-(phenylsulfonyl)cyclohexene (26a). An 850-mg (3.4 mmol) sample of **11** was alkylated with benzyl bromide (0.42 mL, 3.5 mmol), and the crude product was chromatographed on silica gel (20 g). Elution with 10% ethyl acetate in hexane gave 1.02 g (89%) of **26a** as a colorless crystalline solid: mp 98–100 °C (from hexane–ethyl acetate, 10:1); IR (CCl_4) 3050, 2945, 2910, 1446, 1302, 1145, 710, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.63 (m, 2 H), 7.58–7.33 (m, 3 H), 7.15 (s, 5 H), 3.28 (d, J = 13.5 Hz, 1 H), 2.90 (d, J = 13.5 Hz, 1 H), 2.40–1.57 (series of m, 6 H), 1.49 (s, 6 H); MS, M^+ too weak to mass measure.

1,2-Dimethyl-4-benzylcyclohexene (26b). Reductive desulfonylation of **26a** (190 mg, 0.56 mmol) in the conventional manner (1 h, pentane workup) and elution of the product through basic alumina (8 g) with pentane afforded 107 mg (96%) of **26b** as a colorless liquid which was subjected further to VPC (15% SE-30, 140 °C) prior to analysis: IR (neat) 3045, 3012, 2890, 2815, 1605, 1495, 1451, 742, 697; ^1H NMR ($CDCl_3$) δ 7.03 (br s, 5 H), 2.48 (br d, J = 5.5 Hz, 2 H), 2.15–1.36 (series of m, 7 H), 1.55 (s, 6 H); MS, m/e (M^+) calcd 200.1565, obsd 200.1569. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.51; H, 9.93.

1,2-Dimethyl-4-[3-(phenylthio)propyl]-4-(phenylsulfonyl)cyclohexene (27a). An ethanolic sodium ethoxide solution (prepared from 4.6 g of sodium and 30 mL of absolute ethanol) was added to thiophenol (22.0 g, 0.2 mol) dissolved in ethanol (50 mL). This solution was transferred by canula under argon to a solution of 1,3-dibromopropane (60 g) in ethanol (100 mL) over a period of 15 min (exothermic). The reaction mixture was heated to reflux for 1.5 h, benzene (200 mL) was added, and the solution was washed with water and brine before being dried and evaporated. The excess dibromide was removed by distillation (bp 75–83 °C) at 60 torr. 1-(Phenylthio)-3-bromopropane (26.1 g, 59%) was subsequently obtained as a colorless liquid: bp 146–153 °C (5 torr); ^1H NMR ($CDCl_3$) δ 7.23 (m, 5 H), 3.47 (t, J = 7.0 Hz, 2 H), 3.00 (t, J = 7.5 Hz, 2 H), 2.13 (tt, J = 7.5, 7.0 Hz, 2 H).

Alkylation of **11** (750 mg, 3.0 mmol) with the preceding bromide (715 mg) furnished 1.03 g (86%) of **27a**, white solid after silica gel chromatography (elution with 10% ethyl acetate in hexane); IR (CCl_4) 3055, 2920, 1590, 1450, 1302, 1152, 722, 690, 614 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87–7.50 (m, 2 H), 7.60–7.35 (m, 3 H), 7.18 (s, 5 H), 2.85–1.60 (series of m, 12 H), 1.56 (br s, 6 H); MS, M^+ too weak to mass measure.

1,2-Dimethyl-4-[3-(phenylthio)propyl]cyclohexene (27b). Reductive desulfonylation of **27a** (800 mg, 2.0 mmol) according to the general procedure (7 h, pentane workup) and elution of the product through basic alumina (15 g) provided 442 mg (85%) of **27b** as a colorless oil which was subjected further to molecular distillation [bp 142–145 °C (0.5 torr)] prior to analysis: IR (CCl_4) 3058, 2975, 2895, 2845, 2820, 1586, 1480, 1440, 687, 598 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22–6.97 (m, 5 H), 2.83 (t, J = 6.5 Hz, 2 H), 2.23–1.02 (series of m, 11 H), 1.59 (br s, 6 H); MS, m/e (M^+) calcd 260.1599, obsd 260.1593. Anal. Calcd for $C_{17}H_{24}S$: C, 78.40; H, 9.29. Found: C, 78.43; H, 9.14.

1,2-Dimethyl-4-(4-*p*-tolylpentyl)-4-(phenylsulfonyl)cyclohexene (28a). A solution of 4-*p*-tolylpentanoic acid (33.3 g, 0.173 mol) in dry ether (100 mL) was added to a mechanically stirred slurry of lithium aluminum hydride (8.3 g, 0.22 mol) in the same solvent (500 mL). The mixture was refluxed with stirring for 24 h, cooled, and treated with saturated sodium sulfate solution until the salts were white. The inorganic salts were separated by filtration, and the filtrate was washed with water and brine prior to drying. Solvent evaporation gave 30.5 g (99%) of the alcohol which was used directly in the next step.

A solution of the alcohol (30.5 g, 0.171 mol), dihydropyran (21.3 g, 0.254 mol), and *p*-toluenesulfonic acid (0.25 g) in ether (300 mL) was stirred overnight, washed with saturated sodium bicarbonate solution and brine, dried, and evaporated. The resulting tetrahydropyranyl ether was added in one portion at 0 °C to a dichloromethane solution (500 mL) and triphenylphosphine dibromide (from 59.7 g of Br_2 and 97.8 g of Ph_3P) and stirred overnight. The reaction mixture was concentrated by rotary evaporation, taken up in pentane, filtered, and reevaporated. The residue was filtered through alumina (100 g, pentane elution), and the bromide was subsequently isolated by distillation as a colorless liquid [bp 90–94 °C (0.6 torr); 37.0 g (89.8%)] and used directly.

Alkylation of **11** (1.3 g, 5.2 mmol) with the preceding bromide (1.28 g) furnished 1.73 g (81.1%) of **28a** as a colorless viscous oil following silica gel chromatography (elution with 10% ethyl acetate in hexane): IR (CCl_4) 3040, 2945, 2910, 2850, 1512, 1445, 1302, 1144, 720, 590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.62 (m, 2 H), 7.57–7.33 (m, 3 H), 7.03 (s, 4 H), 2.66 (m, 1 H), 2.32 (s, 3 H), 1.57 (br s, 6 H), 2.02–0.87 (series of m, 15 H); MS, M^+ too weak to mass measure.

1,2-Dimethyl-4-(4-*p*-tolylpentyl)cyclohexene (28b). Reductive desulfonylation of **28a** (925 mg, 2.26 mmol) according to the general procedure (5 h, pentane workup) gave 570 mg (93%) of **28b** as a colorless oil following chromatography on basic alumina (pentane elution): IR (neat) 3055, 3005, 2975, 2945, 2890, 1498, 720, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.98 (br s, 4 H), 2.61 (m, 1 H)8 2.28 (s, 3 H), 1.63 (br s, 6 H), 1.20 (d, J = 7.5 Hz, 3 H), 2.05–0.83 (series of m, 13 H); MS, m/e (M^+) calcd 270.2347, obsd 270.2354.

1-Methoxy-6-allyl-6-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (29a). Alkylation of **24** (1.0 g, 3.6 mmol) with allyl bromide (490 mg, 4.0 mmol) as described above provided an endo/exo mixture of **29a** which was chromatographed on silica gel (130 g). Elution with 10% ethyl acetate in hexane afforded the *endo*-allyl isomer in the early fractions: 320 mg; colorless solid; mp 92–94 °C (from hexane–ethyl acetate, 4:1); IR (CCl_4) 3028, 2930, 2812, 1648, 1448, 1302, 1145, 610, 586 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.63 (m, 2 H), 7.53–7.16 (m, 3 H), 6.08 (m, 2 H), 6.13–5.5 (m, 1 H), 5.10–4.76 (m, 2 H), 2.93 (s, 3 H), 2.73–1.10 (series of m, 9 H); MS, m/e (M^+) calcd 318.1290, obsd 318.1295.

Continued elution gave the *exo*-allyl isomer (670 mg) as colorless crystals: mp 93.5–95 °C; IR (CCl_4) 3050, 2930, 2812, 1632, 1445, 1302, 1139, 685, 589 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.70 (m, 2 H), 7.53–7.28 (m, 3 H), 6.00 (m, 2 H)8 6.13–5.78 (m, 1 H), 5.22–4.78

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(m, 2 H), 3.20 (s, 3 H), 2.91–1.20 (series of m, 9 H); MS, M^+ too weak to mass measure.

The total yield of **29a** was 86.5%, and the exo/endo ratio was 2.1:1.

1-Methoxy-6-allylbicyclo[2.2.2]oct-2-ene (29b). Reductive desulfonylation of **29a** (300 mg, 0.943 mmol) according to the general procedure (5 h, pentane workup) gave 150 mg (95%) of **29b** as a colorless liquid after filtration of the crude product through basic alumina (8 g, pentane elution): IR (neat) 3055, 3025, 2920, 2810, 1638, 1090, 905, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.23–5.91 (m, 2 H), 5.88–4.58 (series of m, 3 H), 3.23 (s, 3 H), 2.62–0.87 (series of m, 10 H); MS, m/e (M^+) calcd 178.1358, obsd 178.1362. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.86; H, 10.00.

1-Methoxy-6-(3,7-dimethyl-2,6-octadienyl)-6-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (30a). Alkylation of **24** (1.40 g, 5.04 mmol) with geranyl bromide (1.15 g, 5.3 mmol)[51] was carried out as described above by using HMPA as a cosolvent. The waxy solid residue obtained on workup was filtered through silica gel (25 g, elution with 10% ethyl acetate in hexane) to give **30a** as an endo/exo mixture of isomers: white solid; mp 81–83 °C (from hexane–ethyl acetate, 10:1); IR (CCl_4) 3045, 2925, 2808, 1445, 1310, 1140, 1120, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95–7.6 (m, 2 H), 7.5–7.15 (m, 3 H), 6.25–6.01 (m, 2 H), 5.61–4.82 (m, 2 H), 3.22 and 2.95 (s, 3 H total, ratio 11:3), 2.93–1.05 (series of m, 1o H), 1.68 (s, 3 H), 1.60 (s, 3 H), 1.47 (s, 3 H); MS, m/e (M^+) calcd 414.2228, obsd 414.2234.

1-Methoxy-6-(3,7-dimethyl-2,6-octadienyl)bicyclo[2.2.2]-oct-2-ene (30b). Reductive desulfonylation of **30a** (1.10 g, 2.66 mmol) as before (9 h, benzene workup) and filtration of the crude product through basic alumina (15 g, elution with 5% ethyl acetate in hexane) gave 505 mg (93%) of *exo/endo*-**30b** as a colorless oil: IR (neat) 3035, 2915, 2845, 2808, 1645, 1450, 1100, 738, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.28–5.58 (m, 2 H), 5.03 (br m, 2 H)8 3.30 and 3.23 (s, 3 H total, ratio 5:1), 2.63–0.97 (series of m, 23 H); MS, m/e (M^+) calcd 274.2297, obsd 274.2303. Anal. Calcd for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 82.96; H, 10.75.

1-Methoxy-6-(2,2-diethoxyethyl)-6-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (31a). Alkylation of **24** (1.0 g, 3.60 mmol) with bromoacetaldehyde diethyl acetal (1.0 g, 5.1 mmol) was carried out as described above by using HMPA as a cosolvent. Purification of the product by silica gel chromatography (15 g, elution with 15–20% ethyl acetate in hexane) afforded 910 mg (74%) of **31a** as a colorless viscous liquid: IR (neat) 3050, 2960, 2925, 2820, 1445, 1295, 1125, 1055, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.93–7.63 (m, 2 H), 7.52–7.23 (m, 3 H), 6.21–5.50 (m, 2 H), 5.18 (2 d, J = 6.5 Hz, 1 H total), 3.58 (br q, J = 6.0 Hz, 4 H), 3.17 and 2.90 (s, 3 H total, ratio 73:27), 2.70–0.98 (series of m, 10 H), 1.23 (2 t, 3 H total).

Continued elution returned 95 mg of unreacted **24**. The yield of **31a** based upon recovered starting material is 82%.

1-Methoxy-6-(2,2-diethoxyethyl)bicyclo[2.2.2]oct-2-ene (31b). Reductive desulfonylation of **31a** (600 mg, 1.52 mmol) as before (5 h, benzene workup) and filtration of the crude product through silica gel (18 g, elution with 10% ethyl acetate in hexane) furnished 310 mg (80%) of **31b** as a colorless liquid: IR (neat) 3040, 2920, 2808, 1445, 1110, 1055, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.30–5.98 (m, 2 H), 4.47 (m, 1 H), 3.50 (2 q, 4 H total), 3.30 (s, 3 H), 1.20 (br t, J = 7.5 Hz, 6 H), 2.58–1.47 (series of m, 10 H); MS, m/e (M^+) calcd 209.1541, obsd 209.1546.

1-Methyl-4-(trimethylsilyl)-4-(phenylsulfonyl)cyclohexene (32a). Silylation of **17** (1.46 g, 6.19 mmol) with chlorotrimethylsilane (0.9 mL, 7.1 mmol) according to the general alkylation procedure afforded 1.64 g (86%) of **32a** as a colorless, crystalline solid [mp 96–97 °C (from hexane–ethyl acetate, 10:1)] after silica gel chromatography (20 g, elution with 10% ethyl acetate in hexane): IR (CCl_4) 3060, 3010, 2963, 2905, 2850, 1683, 1445, 1304, 1255, 1145, 848, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80–7.61 (m, 2 H), 7.60–7.40 (m, 3 H), 5.17 (m, 1 H), 2.45 (m, 2 H), 2.32–1.68 (series of m, 4 H), 1.43 (br s, 3 H), 0.32 (s, 9 H); MS, m/e (M^+) calcd 308.1266, obsd 308.1265.

1-Methyl-4-(trimethylsilyl)cyclohexene (32b). Reductive desulfonylation of **32a** (0.97 g, 3.15 mmol) as before (6.5 h, pentane workup) and the customary workup led to the isolation of **32b** (420 mg, 79%) as a colorless liquid. An analytical sample was obtained by preparative VPC (15% SE-30, 120 °C): IR (CCl_4) 3040, 2960, 2905, 2825, 1445, 1435, 1250, 885, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.43 (m, 1 H), 1.72 (br s, 3 H), 1.27–1.21 (m, 6 H), 0.10 (m, 1 H), 0.03 (s, 9 H); MS, m/e (M^+) calcd 168.1334, obsd 168.1337. Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.40; H, 11.95.

1-Methyl-4-[(trimethylsilyl)methyl]-4-(phenylsulfonyl)-cyclohexene (33a). Triflic anhydride (1.41 g, 5.0 mmol) dissolved in 5 mL of dry dichloromethane was cooled to −20 °C under argon, and a solution of pyridine (0.395 g, 5.0 mmol) in the same solvent (5 mL) was added via syringe. The reaction mixture was stirred for 5 min, (trimethylsilyl)methanol (0.525 g, 5.0 mmol) was introduced, and the esterification was allowed to proceed at room temperature for 2 h. Pentane (20 mL) was added, and the mixture was filtered, and the filtrate was eluted through silica gel (8 g, pentane). There was isolated 710 mg (60.1%) of the triflate as a colorless liquid which was used directly.

Alkylation of **17** (1.07 g, 4.53 mmol) with (trimethylsilyl)methyl triflate (0.90 g, 5.03 mmol) according to the general directives and elution of the crude product through silica gel (15 g, 15% ethyl acetate in hexane) gave 1.14 g (78%) of **33a** as a colorless viscous oil: IR (CCl_4) 3060, 3010, 2940, 2890, 2840, 1448, 1302, 1248, 1140, 838, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85–7.63 (m, 2 H), 7.55–7.32 (m, 3 H), 5.17 (m, 1 H), 2.33–1.47 (series of m, 6 H), 1.57 (br s, 3 H), 1.12 (s, 2 H), 0.15 (s, 9 H); MS, M^+ too weak to mass measure.

1-Methyl-4-[(trimethylsilyl)methyl]cyclohexene (33b). Reductive desulfonylation of **33a** (920 mg, 2.86 mmol) as before (7 h, pentane workup) and filtration through silica gel (10 g, pentane elution) furnished 480 mg (92%) of **33b** as a colorless oil. An analytical sample was obtained by preparative VPC (15% SE-30, 120 °C): IR (neat) 3020, 3000, 2940, 2890, 2860, 1658, 1446, 1435, 1248, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.38 (m, 1 H), 2.51–1.02 (series of m, 10 H), 0.68 (m, 2 H), 0.18 (s, 9 H); MS, m/e (M^+) calcd 182.1491, obsd 182.1495. Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.15. Found: C, 72.29; H, 11.75.

1-Methyl-4-(2-tetrahydrofuryl)-4-(phenylsulfonyl)cyclohexene (34a). The 2-(iodomethyl)tetrahydrofuran [bp 97–100 °C (17 torr)] was prepared from the chloro derivative by the method of Ford-Moore.[52] The alkylation of **17** (960 mg, 4.07 mmol) with this electrophile (750 mg, 4.44 mmol) was conducted with HMPA as a cosolvent. Following chromatography on silica gel (25 g, elution with 20% ethyl acetate in hexane), there was isolated 810 mg 72.9% based on recovered **17**) of **34a** as colorless crystals: mp 91–96.5 °C (from hexane–ethyl acetate, 9:1); IR (CCl_4) 3055, 3010, 2960, 2925, 2860, 1678, 1448, 1296, 1140, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98–7.72 (m, 2 H), 7.68–7.20 (m, 3 H), 5.32 (m, 1 H), 4.35 (2 quintuplets, J = 5.5 Hz, 1 H), 3.71 (2 t, J = 6.0 Hz, 2 H), 2.73–0.82 (series of m, 15 H); MS, m/e (M^+) calcd 178.1358, obsd 178.1366.

1-Methyl-4-(2-tetrahydrofurfuryl)cyclohexene (34b). Reductive desulfonylation of **34a** (750 mg, 2.34 mmol) in the predescribed manner (4.5 g, pentane workup) led after silica gel chromatography (10 g, elution with 10% ethyl acetate in hexane) to the isolation of **34b** as a colorless liquid: IR (neat) 3020, 2960, 2910, 1760, 1440, 1065 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.37 (m, 1 H), 4.04–3.51 (m, 3 H), 2.57–0.75 (series of m, 13 H), 1.63 (br s, 3 H); MS, m/e (M^+) calcd 180.1514, obsd 180.1519. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.76; H, 11.09.

1-Methyl-4-(4-carbethoxybutyl)-4-(phenylsulfonyl)-cyclohexene (35a). The ethyl 5-iodovalerate [bp 73–75 °C (0.3 torr)] was prepared from the chloro derivative by the method of Ford-Moore:[52] 80.1% yield; ^1H NMR ($CDCl_3$) δ 4.08 (q, J = 7.5 Hz, 2 H), 3.20 (t, J = 6.5 Hz, 2 H), 2.32 (t, J = 6.5 Hz, 2 H), 1.77 (m, 4 H), 1.28 (t, J = 7.5 Hz, 3 H).

The alkylation of **17** (1.3 g, 5.5 mmol) with ethyl 5-iodovalerate (1.8 g, 7.0 mmol) was performed under inverse addition conditions and with HMPA as a cosolvent. Chromatography on silica gel (30 g, elution with 10% ethyl acetate in hexane) gave 1.43 g (87% based upon recovered **34**) of **35a** as a colorless oil: IR (CCl_4) 3050, 2960, 2920, 1735, 1445, 1300, 1140, 902, 715, 688 cm^{-1}; ^1H NMR

(51) For the general procedure, see: Stork, G.; Grieco, P. A.; Gregson, M. *Org. Synth.* **1974**, *54*, 68.

(52) Ford-Moore, A. H. "Organic Syntheses"; Wiley: New York, 1963; Collect. Vol. IV, p 84.

($CDCl_3$) δ 7.93–7.62 (m, 2 H), 7.61–7.36 (m, 3 H), 5.22 (m, 1 H)8, 4.07 (q, J = 7 Hz, 2 H), 2.55–1.12 (series of m, 17 H), 1.25 (t, J = 7 Hz, 3 H).

1-Methyl-4-(4-carbethoxybutyl)cyclohexene (35b). Reductive desulfonylation of **35a** (740 mg, 2.03 mmol) in the usual manner (3.5 h, ether workup) followed by filtration through silica gel (12 g, elution with 10% ethyl acetate in hexane) gave 370 mg (81.4%) of **35b** as a colorless, pleasant smelling oil: IR (neat) 3040, 2950, 2905, 2860, 2840, 2820, 1738, 1445 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.30 (m, 1 H), 4.07 (q, J = 6.5 Hz, 2 H), 1.63 (br s, 3 H), 1.27 (t, J = 6.5 Hz, 3 H), 2.58–0.87 (series of m, 15 H); MS, m/e (M^+) calcd 224.1776, obsd 224.1780. Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.30; H, 10.63.

Cycloaddition of 2 to Cyclopentadiene. Freshly cracked cyclopentadiene (1.92 g, 29 mmol) and **2** (1.20 g, 5.0 mmol) in benzene (5 mL) were stirred at ambient temperature for 3.5 days. The solvent was evaporated, and the majority of the dicyclopentadiene was removed by heating to 50 °C in vacuo for 2 h. The residual oil was chromatographed on silica gel; following elution with pentane (500 mL), 5% ethyl acetate in hexane was employed. The early fractions contained **36** and the latter ones **37**. The total yield was 1.36 g (89%) and the ratio 2:1, respectively.

For **36**: colorless crystals; mp 49–50 °C (from hexane); ^1H NMR (CCl_4) δ 7.95–7.45 (m, 5 H), 6.30 (dd, J = 5, 3 Hz, 1 H), 5.87 (dd, J = 5, 3 Hz, 1 H), 3.47 (dd, J = 6, 3 Hz, 1 H), 2.90 (br s, 2 H), 1.40–1.03 (m, 3 H), 0.13 (s, 9 H); MS, m/e (M^+) calcd 306.1110, obsd 306.1105. Anal. Calcd for $C_{16}H_{22}O_2SSi$: C, 62.70; H, 7.23. Found: C, 62.83; H, 7.31.

For **37**: mp 110–110.5 °C (from hexane); ^1H NMR (CCl_4) δ 8.00–7.40 (m, 5 H), 6.17 (dd, J = 6, 2.5 Hz, 1 H), 5.90 (dd, J = 6, 3 Hz, 1 H), 3.07 (m, 1 H), 2.93 (m, 1 H), 2.76 (d, J = 6 Hz, 1 H), 1.97 (d, J = 9 Hz, 1 H), 1.73 (dd, J = 6, 3 Hz, 1 H), 1.40 (d, J = 9 Hz, 1 H), 0.00 (s, 9 H); MS, M^+ too weak to mass measure. Anal. Calcd for $C_{16}H_{22}O_2SSi$: C, 62.70; H, 7.23. Found: C, 62.82; H, 7.29.

Cycloaddition of 3 to Cyclopentadiene. (A) Room-Temperature Conditions. A solution of cyclopentadiene (0.5 g, 7.6 mmol) and **3** (180 mg containing 17% of **2**, 0.62 mmol of **3**) in benzene (3 mL) was stirred at room temperature for 2.5 weeks. A workup as described above including chromatography gave **38** (30%) as colorless plates: mp 114–115 °C (from hexane); ^1H NMR (CCl_4) δ 8.05–7.35 (m, 5 H), 6.24 (dd, J = 5, 3 Hz, 1 H), 5.75 (dd, J = 5, 3 Hz, 1 H), 2.96 (m, 2 H), 2.67 (s, 1 H), 1.93 (d, J = 9 Hz, 1 H), 1.27 (d, J = 9 Hz, 1 H), 0.97 (dd, J = 9, 2 Hz, 1 H), 0.30 (s, 9 H); MS, m/e ($M^+ - CH_3$) 291.0875, obsd 291.0883. Anal. Calcd for $C_{16}H_{22}O_2SSi$: C, 62.70; H, 7.23. Found: C, 62.69; H, 7.24.

(B) In Heated Benzene Solution. A magnetically stirred solution of cyclopentadiene (0.40 g, 6.1 mmol) and **3** (0.50 g, 2.1 mmol) in benzene (3 mL) was heated at 55 °C under nitrogen for 3.5 days with addition of fresh diene (0.4 g) every 12–18 h. Following an identical workup, 370 mg (58%) of pure **38** was isolated.

1,3-Diphenylisobenzofuran Additions to 36–38. A solution of **36** (306 mg, 1.0 mmol) and 1,3-diphenylisobenzofuran (300 mg, 1.11 mmol) in benzene (5 mL) was heated at the reflux temperature under nitrogen in a foil-wrapped flask for 60 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 486 mg (85%) of **39** as colorless cubes: mp 238–239 °C (from chloroform–petroleum ether); ^1H NMR ($CDCl_3$) δ 8.0–7.0 (m, 19 H), 3.37 (m, 2 H), 2.72–2.48 (m, 2 H), 2.30 (m, 2 H), 1.35 (dd, J = 6, 2 Hz, 1 H), 0.70 (d, J = 9 Hz, 1 H), –0.02 (s, 9 H); MS, m/e ($M^+ - CH_3$) calcd 561.1920, obsd 561.1937.

Comparable treatment of **37** (306 mg) under identical conditions afforded 490 mg (85%) of **40** as white cubes: mp 127–129 °C (from petroleum ether); ^1H NMR (CCl_4) δ 7.85–6.75 (m, 19 H), 2.66 (d, J = 7 Hz, 1 H), 2.45–2.15 (m, 4 H), 1.95 (d, J = 7 Hz, 1 H), 1.50 ndd, J = 7, 3 Hz, 1 H), 1.25 (d, J = 10 Hz, 1 H), 0.15 (s, 9 H). Anal. Calcd for $C_{36}H_{36}O_3SSi$: C, 74.96; H, 6.29. Found: C, 74.56; H, 6.30.

Analogous reaction of **38** (200 mg) gave a crude product which partially decomposed upon attempted purification by silica gel chromatography. Although the ^1H NMR spectrum of the crude product indicated essentially quantitative conversion to **41**, there was recovered only 30 mg of this adduct as white cubes: mp 255–256 °C dec; ^1H NMR ($CDCl_3$) δ 7.96–6.73 (series of m, 19 H), 3.10 (m, 1 H), 2.49–2.01 (m, 4 H), 1.56–1.04 (m, 3 H), 0.16 (s, 9 H). This isomer underwent retrograde Diels–Alder fragmentation in the mass spectrometer.

Conversion to 42. (A) A solution of **39** (100 mg, 0.174 mmol) and anhydrous tetra-*n*-butylammonium fluoride (1 mL of 1 M solution) in dry tetrahydrofuran (4 mL) was heated at reflux with stirring for 3.5 days. The reaction mixture was poured into water (25 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried, filtered, and evaporated, and the residue was purified by chromatography on silica gel (elution with petroleum ether). A quantitative yield of **42** [mp 202.5–204 °C (lit.[5c] mp 198–200 °C)] was obtained.

(B) Comparable treatment of **40** (109 mg, 0.189 mmol) gave **42** in 91% yield.

(C) Treatment of crude **41** (116 mg, 0.202 mmol) in a comparable manner afforded **42** in 72% yield.

2,3:5,6-Dibenzo-*trans*-7-(trimethylsilyl)-8-(phenylsulfonyl)bicyclo[2.2.2]octadiene (43). A solution of anthracene (0.50 g, 2.8 mmol) and **1** (0.24 g, 1.0 mmol) in toluene was heated at 160 °C in a sealed glass tube for 1 week. After cooling, the mixture was filtered, the solid residue was washed several times with benzene, and the combined filtrates were evaporated. The residue was purified by silica gel chromatography (elution with ethyl acetate–petroleum ether, 1:9). There was obtained 0.41 g (98%) of **43** as colorles crystals: mp 113–114 °C (from hexane); ^1H NMR (CCl_4) δ 7.8–7.0 (m, 13 H), 4.63 (d, J = 3 Hz, 1 H), 4.37 (d, J = 2 Hz, 1 H), 3.58 (dd, J = 9, 3 Hz, 1 H), 1.73 (dd, J = 9, 2 Hz, 1 H), –0.07 (s, 9 H); MS, m/e (M^+) calcd 418.1423, obsd 418.1409. Anal. Calcd for $C_{25}H_{26}O_2SSi$: C, 71.73; H, 6.26. Found: C, 71.54; H, 6.25.

Dibenzobarrelene (45a). Adduct **43** (44 mg, 0.105 mmol) was added to a solution of tetra-*n*-butylammonium fluoride in tetrahydrofuran (0.18 mL of 1 M solution) in the same solvent (3 mL). The reaction mixture was heated at the reflux temperature with stirring for 1 h and worked up in the predescribed manner. After chromatography on silica gel (elution with petroleum ether), there was isolated 84% of **45a**, identical in all respects with an authentic sample.

2,3:5,6-Dibenzo-*trans*-7-(trimethylsilyl)-8-(phenylsulfonyl)bicyclo[2.2.2]octadiene-*8-d* (44). To a magnetically stirred solution of **43** (0.50 g, 1.20 mmol) in dry tetrahydrofuran (30 mL) maintained under a nitrogen atmosphere was added *n*-butyllithium in hexane (2 mL of 1.5 M solution, 2.5 equiv). After 30 min, deuterium oxide (1 mL) was introduced, and stirring was continued for 30 min before the reaction mixture was poured into water (50 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with water (2 × 30 mL), dried, and evaporated. Silica gel chromatography as before afforded 0.41 g (82%) of **44**: ^1H NMR (CCl_4) δ 7.8–7.0 (m, 13 H), 4.63 (s, 1 H), 4.37 (d, J = 2 Hz, 1 H), 1.73 (d, J = 2 Hz, 1 H), –0.07 (s, 9 H); MS, m/e (M^+) calcd 419.1485, obsd 419.1473.

Dibenzobarrelene-*7-d* (45b). Reaction of **44** (0.28 g, 0.668 mmol) with tetra-*n*-butylammonium fluoride (2 mL of 1 M solution in THF) in tetrahydrofuran (3 mL) in the customary fashion gave **45b** (0.10 g, 73%) as white needles: ^1H NMR (CCl_4) δ 7.3–6.6 (m, 9 H), 4.90 (m, 2 H); MS, m/e (M^+) calcd 205.1002, obsd 205.1007.

Dibenzobarrelene-*7,8-d*$_2$ (47). Cycloaddition of **8** (0.22 g, 091 mmol) of anthracene (0.50 g, 2.8 mmol) in toluene solution (sealed tube, 160 °C, 9.5 days) in the predescribed manner produced **46** as colorless plates: 368 mg (96.5%); ^1H NMR (CCl_4) δ 7.8–7.0 (m, 13 H), 4.63 (s, 1 H), 4.37 (s, 1 H), –0.07 (s, 9 H).

Heating of **46** (143 mg, 0.34 mmol) with tetra-*n*-butylammonium fluoride (2 mL of 1 M solution in THF) in tetrahydrofuran (3 mL) as before provided 49.7 mg (71%) of **47** as white needles: mp 119.5–120.5 °C (from ethanol–water); ^1H NMR (CCl_4) δ 7.23–6.55 (m, 8 H), 4.90 (m, 2 H).

Methylation of 43. A stirred solution of **43** (0.50 g, 1.2 mmol) in dry tetrahydrofuran (10 mL) was treated under nitrogen with *n*-butyllithium in hexane (2.55 mL of 1.5 M solution, 3.2 equiv). After 30 min, methyl iodide (0.5 mL, 6 equiv) was added, and alkylation was allowed to proceed for 30 min before the reaction mixture was poured into water and the product extracted with dichloromethane. The combined organic layers were washed with water, dried, and evaporated. The residue was purified by MPLC

on silica gel (elution with 9% ethyl acetate in petroleum ether) to give a mixture of **48a** and **49a** (85%). Recrystallization from ethyl acetate–petroleum ether and subsequently from ether furnished the more polar isomer in analytically pure form: colorless crystals; mp 181–182 °C; ^{1}H NMR ($CDCl_3$) δ 8.0–7.0 (m, 13 H), 4.51 (d, J = 1.8 Hz, 1 H), 4.41 (s, 1 H), 2.21 (d, J = 1.8 Hz, 1 H), 1.50 (s, 3 H), 0.09 (s, 9 H); MS, m/e (M^+) calcd 432.1579, obsd 432.1590. Anal. Calcd for $C_{26}H_{28}O_2SSi$: C, 72.18; H, 6.52. Found: C, 71.97; H, 6.51.

The less polar isomer exhibited the following ^{1}H NMR spectral data ($CDCl_3$): δ 7.95–7.01 (m, 13 H), 4.41 (d, J = 1.6 Hz, 1 H), 4.36 (s, 1 H), 2.13 (d, J = 1.6 Hz, 1 H), 1.28 (s, 3 H), −0.14 (s, 9 H).

7-Methyldibenzobarrelene (50a). A magnetically stirred solution of the more polar isomer **48a** or **49a** (33.4 mg, 0.077 mmol) and tetra-*n*-butylammonium fluoride (1 mL of 1 M solution in THF) in dry tetrahydrofuran was heated at the reflux temperature under nitrogen for 30 min. The usual workup afforded 16.2 mg (71%) of **50a** after silica gel chromatography (elution with petroleum ether). The analytical sample (mp 107–108 °C) was obtained by preparative VPC (12 ft × 0.25 in. 5% SE-30, 180 °C): ^{1}H NMR ($CDCl_3$) δ 7.31–6.92 (m, 8 H), 6.51 (ddq, 1 H), 5.02 (d, J = 6 Hz, 1 H), 4.80 (d, J = 1.8 Hz, 1 H), 1.96 (d, J = 1.7 Hz, 3 H). Anal. Calcd for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.50; H, 6.47.

When the less polar isomer was treated analogously, **50a** was produced with equal efficiency. Hydrocarbon **50a** can be conveniently prepared in 58% overall yield from **43** if intermediates are not purified.

Prenylation of 43. From 0.50 g (1.2 mmol) of **43**, excess prenyl bromide (1 mL), and *n*-butyllithium (2.55 mL of 1.5 M solution in hexane) there was isolated after reaction as above an 80% yield of a crude **48b**/**49b** mixture. Because attempts at chromatographic purification caused decomposition, this material was subjected to elimination without further handling.

7-Prenyldibenzobarrelene (50b). The preceding material (96.3 mg, 0.198 mmol) dissolved in dry tetrahydrofuran (2 mL) was heated under nitrogen for 1 h with tetra-*n*-butylammonium fluoride. The usual workup gave **50b** (44 mg, 82%) as a colorless oil which decomposed slowly upon standing: ^{1}H NMR ($CDCl_3$) δ 7.28–6.91 (m, 8 H), 6.45 (m, 1 H) 5.11–5.0 (m, 2 H), 4.80 (d, J = 1.5 Hz, 1 H), 2.95 (d, J = 7 Hz, 2 H), 1.69 (s, 3 H), 1.58 (s, 3 H); MS, m/e (M^+) calcd 272.1467, obsd 272.1516.

The direct conversion of **43** to **50b** proceeds in 63% overall yield.

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Registry No. **1**, 5535-48-8; **2**, 64489-06-1; **3**, 64489-07-2; **4**, 4837-01-8; **5**, 1822-73-7; **6**, 64489-03-8; **7**, 32501-93-2; **8**, 87568-19-2; *exo*-**9**, 19242-75-2; *endo*-**9**, 19285-87-1; *exo*-**10**, 73301-13-0; *endo*-**10**, 73346-62-0; **11**, 73301-14-1; **12**, 73301-18-5; **13**, 498-66-8; **14**, 931-64-6; **15**, 1674-10-8; **16**, 5675-64-9; **17**, 73301-15-2; **18**, 640-57-3; **19**, 87637-85-2; **20**, 87568-20-5; **21**, 87637-86-3; **22**, 73301-16-3; **23**, 73301-20-9; *exo*-**24**, 73301-17-4; *endo*-**24**, 87637-87-4; **25**, 25489-02-5; **26a**, 73301-21-0; **26b**, 73301-29-8; **27a**, 87568-21-6; **27b**, 87568-22-7; **28a**, 73301-23-2; **28b**, 73301-31-2; *exo*-**29a**, 87637-88-5; *endo*-**29a**, 87637-90-9; *exo*-**29b**, 87637-89-6; *endo*-**29b**, 87637-91-0; *exo*-**30a**, 87638-49-1; *endo*-**30a**, 87637-93-2; *exo*-**30b**, 87637-92-1; *endo*-**30b**, 87637-94-3; *exo*-**31a**, 87637-95-4; *endo*-**31a**, 87637-97-6; *exo*-**31b**, 87637-96-5; *endo*-**31b**, 87638-50-4; **32a**, 73301-26-5; **32b**, 39178-72-8; **33a**, 73301-27-6; **33b**, 73301-36-7; **34a**, 73301-25-4; **34b**, 73301-35-6; **35a**, 73301-28-7; **35b**, 73301-37-8; **36**, 82201-44-3; **37**, 82262-88-2; **38**, 82262-89-3; **39**, 82209-55-0; **40**, 82263-28-3; **41**, 82263-29-4; **42**, 10211-14-0; **43**, 82201-45-4; **44**, 82201-47-6; **45a**, 2734-13-6; **45b**, 82201-50-1; **46**, 87585-84-0; **47**, 82209-56-1; **48a**, 82201-48-7; **48b**, 82201-49-8; **49a**, 87568-23-8; **49b**, 87568-24-9; **50a**, 82201-51-2; **50b**, 82201-52-3; PhSNa, 930-69-8; $BrCH_2CH_2Br$, 106-93-4; $BrCH_2CH_2CH_2Br$, 109-64-8; $Me_3SiCH{=}CH_2$, 754-05-2; $PhSO_2Cl$, 98-09-9; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}CHC(CH_3){=}CH_2$, 106-95-6; $CH_2{=}CHCH_2Br$, 106-95-6; Me_3SiCH_2OH, 3219-63-4; Me_3SiCH_2OTf, 64035-64-9; $I(CH_2)_4COOC_2H_5$, 41302-32-3; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; nopadiene, 473-00-7; myrcene, 123-35-3; 2,3-dihydroanisole, 2161-90-2; 1-(phenylthio)-3-bromopropane, 3238-98-0; 4-*p*-tolylpentanoic acid, 26232-97-3; 4-*p*-tolylpentanol, 19876-64-3; 4-*p*-tolylpentanol THP ether, 87568-25-0; 4-*p*-tolylpentyl bromide, 19872-53-8; geranyl bromide, 6138-90-5; bromoacetaldehyde diethyl acetal, 2032-35-1; 2-(iodomethyl)tetrahydrofuran, 5831-70-9; 1,3-diphenylisobenzofuran, 5471-63-6.

Regiocontrolled Synthesis of Mono-, Di-, and Trisubstituted Cyclohexenones by Cycloaddition of Vinyl Sulfones to 1-Methoxy-3-[(trimethylsilyl)oxy]-1,3-butadienes. Conversion of Alkenes into Effective Dienophilic Reagents

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Cycloaddition of phenyl vinyl sulfone to Danishefsky's diene followed by direct ketalization provided **7**, a synthon for the 4-(2-cyclohexenyl) anion. Thus, **7** readily undergoes regiospecific γ-alkylation. Ensuing reductive desulfonylation and hydrolysis provides 2-(and 3-)cyclohexenones efficiently. Zingiberenol, a monocyclic sesquiterpene, was prepared by means of this methodology. Terminal alkenes and cyclic olefins enter into comparable regiocontrolled Diels–Alder addition if they are first subjected to selenosulfonation and oxidation to the vinyl sulfone. Removal of the phenylsulfonyl substituent after condensation provides the adducts which are formally derived from alkylation of the hypothetical C_5 anion of 2-cyclohexenone. The scheme can be expanded to include γ-alkylation prior to desulfonylation. By this means, one is able to prepare 4,5-disubstituted 2-(and 3-)cyclohexenones where the nature of the pendant side chains can be widely varied.

As a group, 2-cyclohexenones comprise an important class of starting materials for the synthetic chemist. Although their utilization in a myriad of contexts has evolved systematically over the years, complications continue to persist during attempts to functionalize such α,β-unsaturated ketones at specific sites. While their kinetic enolates, generalized by **1**, commonly allow for clean α'-alkylation,[1] thermodynamic enolates, e.g., **2**, have proven more difficult

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