

was collected, 1720 of them [$I > 3\sigma(I)$] were considered observed and used in structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix anisotropic least-squares techniques. Hydrogen atoms were refined with the constraint C-H = 1.08 Å. The final R index was 0.074 ($R_w = 0.082$, $\omega = 1/\sigma^2(F)$).

X-ray Crystal Structure Analysis of 13. Crystal data: $C_{10}H_9Cl_4NO_2S$, $M = 349.1$, monoclinic, $a = 14.264$ (8) Å, $b = 8.128$ (6) Å, $c = 12.356$ (7) Å, $\beta = 106.76$ (7)°, $Z = 4$, $D_c = 1.69$ g cm⁻³, space group $P2_1/n$. Intensity data were measured up to 70° by the $\omega - 2\theta$ step-scanning mode with Ni-filtered Cu K α radiation ($\lambda = 1.5418$ Å). A total of 2912 reflections was collected and 2230 with $I > 2\sigma(I)$ were used in the analysis. The structure was solved by direct methods and refined by full-matrix anisotropic least-squares techniques. Hydrogen atoms were refined with the

constraint C-H = 1.08 Å. The final R index was 0.054 ($R_w = 0.063$, $\omega = 1/\sigma^2(F)$).

Registry No. 1a, 288-47-1; 1b, 693-95-8; 1c, 3581-89-3; 1d, 15679-09-1; 1e, 15679-10-4; 2a, 87830-79-3; 2c, 87830-80-6; 3a, 79265-40-0; 3c, 87830-81-7; 4a, 79265-41-1; 4b, 87830-82-8; 4c, 87830-83-9; 7a, 87830-84-0; 8a, 87830-85-1; 9a, 87830-86-2; 10a, 87636-20-2; 10b, 24295-03-2; 11, 87830-87-3; 12, 87830-88-4; 13, 87841-56-3; 14, 87830-89-5; 15, 87830-90-8; 16, 87830-91-9; TBCK, 29342-22-1; DCK, 4591-28-0; DPK, 525-06-4.

Supplementary Material Available: Tables of atomic coordinates, bond distances, and bond angles of cycloadducts 2a and 13 (5 pages). Ordering information is given on any current masthead page.

(Z)- and (E)-1,2-Bis(phenylsulfonyl)ethylenes as Synthetic Equivalents to Acetylene as Dienophile

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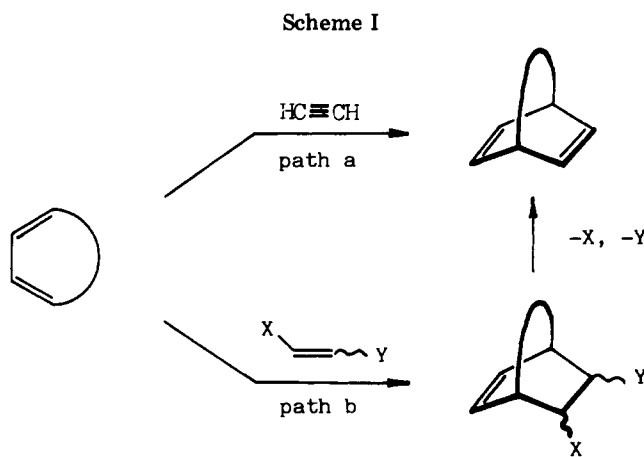
Received August 11, 1983

A new method for introducing an ethylenic bridge via a cycloaddition reaction has been developed. It makes use of either (Z)- or (E)-1,2-bis(phenylsulfonyl)ethylene (5 or 6) as synthetic equivalents of acetylene. The high activation due to the two sulfonyl groups promotes cycloaddition even to very unreactive dienes. The removal of the two sulfonyl groups for the required formation of the carbon-carbon double bond is promoted by reduction with metal amalgams in high yields. These properties, associated with the stability of the reagents and the ease of performance of the reactions, make this method a very useful synthetic tool for the preparation of polycyclic dienes and a valid alternative to the commonly available reagents that largely depend upon oxidative methods.

The synthesis of cyclic and polycyclic 1,4-dienes has been attracting the attention of several research groups for many years as they are important building blocks for the preparation of complex molecules. In fact the reactivity of these homodienes is of practical and theoretical interest in view of the forced conformation imposed by the cyclic or polycyclic arrangement. Depending upon the degree of conjugation of the two carbon-carbon double bonds, this class of dienes can experience [2 + 2] intramolecular, photochemical cycloaddition, di- π -methane (Zimmerman) rearrangement, complexation with metals, and a variety of structural rearrangements.

As shown in Scheme I, the most direct approach to the synthesis of these 1,4-dienes is the [4 + 2] cycloaddition of acetylene to 1,3-dienes. However, due to the low dienophilic reactivity of the triple bond as well as the hazards involved in handling acetylene under pressure and at high temperatures, this direct route can be used only with the most reactive dienes. As a consequence, several alternative procedures have been devised that are based on the use of acetylene equivalents (path b in Scheme I). These are characterized by a high dienophilic reactivity and by the fact that the activating groups can be readily removed to introduce the second carbon-carbon double bond in the molecule. Indeed, it is this second property that limits the scope of this synthetic approach.

According to the Hendrickson model,¹ the activating groups can be eliminated through oxidative, isohypsic, or reductive processes. The most common acetylene equiv-



alents (maleic anhydride, fumaric and maleic acid derivatives, etc.) belong to the first class, but most of the several oxidation methods available²⁻⁵ present intrinsic drawbacks. Isohypsic acetylene equivalents⁶⁻⁸ (acrylic acid derivatives,

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(3) Criegee, R. "Oxidation in Organic Chemistry"; Wiberg, K. B. Ed.; Academic Press: New York, 1965; Part A, p 278. Rubottom, G. M. "Oxidation in Organic Chemistry"; Trahanovsky, W. S. Ed.; Academic Press: New York, 1982; Part D, pp 81-89.

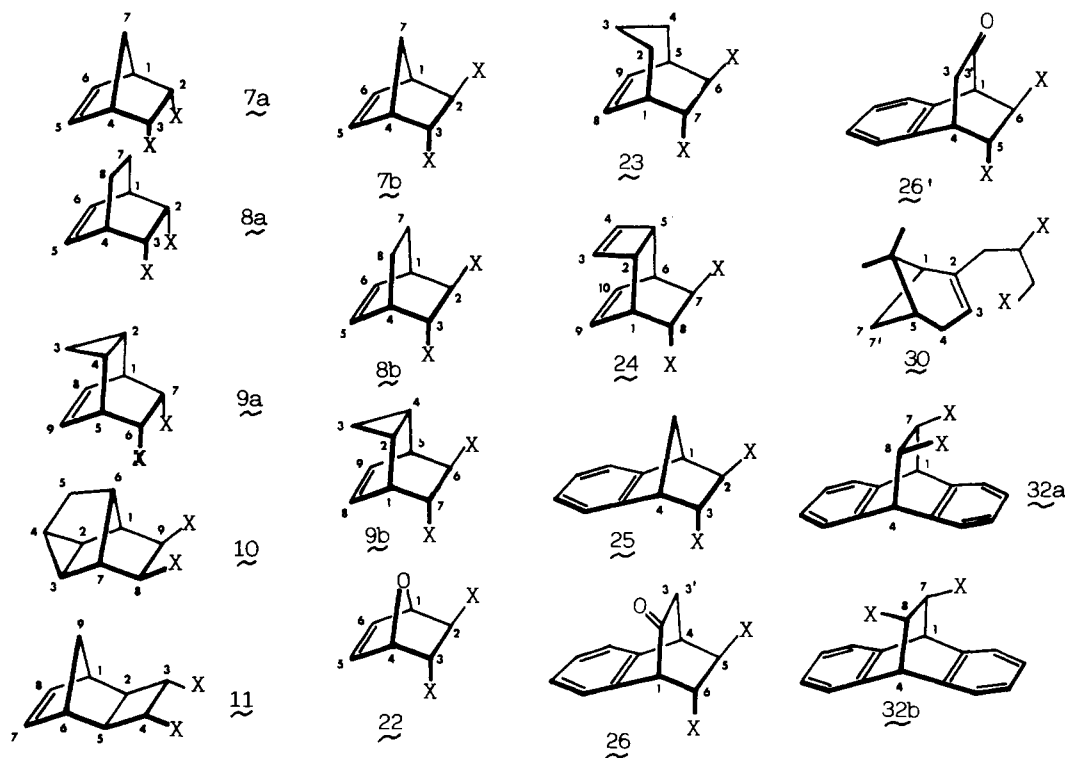
(4) Radlick, P.; Klem, R.; Spurlock, S.; Sims, J. J.; van Tamelen, E. E.; Whitesides, T. *Tetrahedron Lett.* 1968, 5117. Westberg, H. H.; Dauben, Jr., H. J. *Ibid.* 1968, 5123.

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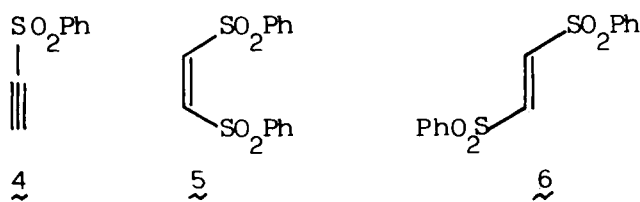
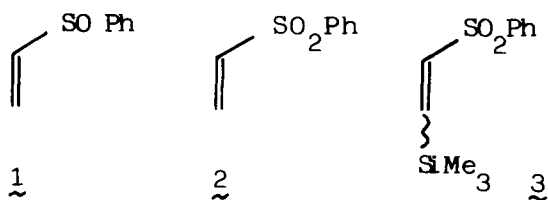
(1) Hendrickson, J. B. *J. Am. Chem. Soc.* 1971, 93, 6847.

Chart I



acetylene dicarboxylate, norbornadiene, etc.) present synthetic difficulties or require high temperatures for the removal of the activating functionalities, and the reductive acetylene equivalents⁹ (vinylene carbonate, halogenolefins, etc.) are among the less reactive dienophiles.

To circumvent the drawbacks encountered with reagents activated with carbonyl groups, a number of acetylene equivalents have recently been used which entail the activation by sulfur functionalities such as sulfoxides and sulfones. For example, vinyl sulfoxide (1) has been shown

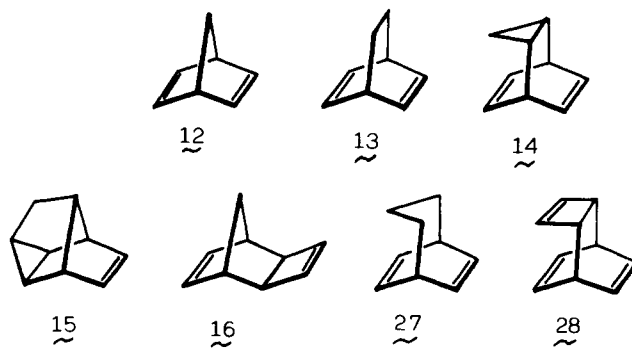


by Paquette and Magnus¹⁰ to be a convenient reagent, but its use is limited to very reactive dienes. The higher reactivity shown by the sulfone analogue 2¹¹ cannot be utilized because of the lack of an easy method to form the

carbon-carbon double bond from sulfones. For this reason, reagent 3 has been devised,¹² but the advantage gained in the eliminative step with the introduction of the silyl group was offset by the poorer dienophilic reactivity. Alternatively, the ethynyl sulfone (4)¹³ can be used but with a drawback due to the lower dienophilic reactivity of acetylenic compounds with respect to the ethylenic ones. The use of doubly sulfonyl-activated olefins of the type 5 and 6 was not taken into consideration because of the lack of a method to convert the adducts into the desired olefin.

Recently, we reported that 1,2-bis(phenylsulfonyl)ethanes can be reduced with sodium amalgam in methanol to give the corresponding olefins and hence we opened the way to the use of the sulfone 5 as an acetylene equivalent.¹⁴

Indeed, the value of this synthetic concept was initially demonstrated with the cycloaddition of 5 to cyclopentadiene, cyclohexadiene, cycloheptatriene, norbornadiene, and quadricyclane, all affording the expected cycloadducts 7a-11a (see Chart I). After reduction with sodium amalgam in methanol, these adducts gave the desired 1,4-dienes 12-16.



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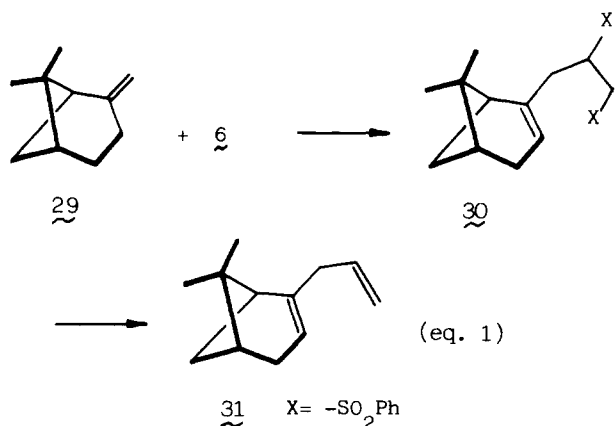
Table I. Reaction Conditions, Yields, and Physical Constants for the Cycloadducts Derived by (*Z*)-1,2-Bis(phenylsulfonyl)ethylene (5)

cyclo-adduct	solvent	temp, °C	t, h	yield, %	mp, ^a °C	recrystallization solvent	microanal C, H found (calcd)
7a	CH ₂ Cl ₂	25	3	98	263-264 ^b	CH ₂ Cl ₂	
8a	toluene	111	14	91	304-306 ^c	toluene	62.06 (61.83), 5.02 (5.19)
9a	toluene	111	14	92	266-268	toluene	62.59 (62.97), 5.14 (5.03)
10a	toluene	111	24	92	334-336	CH ₂ Cl ₂	
11a	CH ₂ Cl ₂	25	120	93	261-263	CHCl ₃	
32a	neat	160	18	46	268-270	CH ₂ Cl ₂ /EtOEt ^d	61.46 (60.94), 4.31 (4.23) ^e

^a With partial decomposition. ^b Lit.³⁷ mp 240-249 °C (C₆H₆/EtOH). ^c Lit.^{19b} mp 289 °C (dioxane). ^d Dissolved in the minimum amount of CH₂Cl₂ and ether added. ^e Calculated for C₂₂H₂₄Cl₂O₄S₂ since it crystallizes with one molecule of CH₂Cl₂.

Furthermore we confirmed¹⁵ the higher reactivity of the *E* isomer 6 and showed that the adducts are equally labile towards reductive elimination. In fact, while less conventional dienes like furane (17), cycloheptadiene (18), cyclooctatetraene (COT) (19), indene (20), and β -naphthol (21) proved to be unreactive toward 5, they provided the expected cycloadducts 22-26 in good yields and the dienes 27 and 28 upon reductive elimination.¹⁶

Finally, to expand the utilization of this reagent, we used it in the ene reaction with β -pinene (29), to afford the adduct 30 which gave 31 on reduction (eq 1). To the best



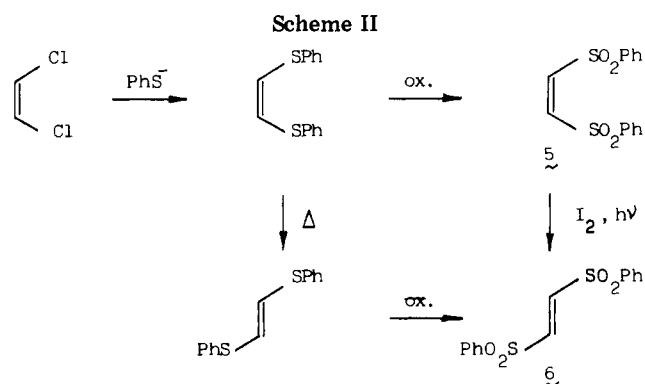
of our knowledge, this last example does not have precedent in the literature.

Herein we report in full on our work with sulfones 5 and 6 as acetylene equivalents. Specifically we report on the range of dienes that can be used, on the stereochemistry of addition determined by NMR analysis of the adducts, and on the study of the elimination of the sulfonyl groups to give the desired unsaturated polycyclic molecules.

Results and Discussion

Synthesis of (*Z*)- and (*E*)-1,2-Bis(phenylsulfonyl)ethylenes (5 and 6). The extended work by Truce et al.¹⁷ on the reaction of phenylthiolate anion with chloroethylenes is the basis for the preparation of the dienophiles. Reaction of the commercially available (*Z*)-1,2-dichloroethylene or of the cheaper (*Z*)- and (*E*)-dichloroethylene mixture (as the *E* isomer does not react) with phenylthiolate gives in almost quantitative yields (*Z*)-1,2-bis(phenylthio)ethylene which upon oxidation furnishes 5 (Scheme II).

The *E* isomer 6 may be obtained by the known thermal isomerization of (*Z*)-1,2-bis(phenylthio)ethylene and subsequent oxidation or better by exposing a sample of 5 in CH₂Cl₂ with a small amount of iodine to the sun light.



Owing to the large difference in solubility between 5 and 6 the *E* isomer nicely separates out of the reaction mixture thus driving the reaction to completion.

Cycloaddition Reaction of (*Z*)-1,2-Bis(phenylsulfonyl)ethylene (5). The high dienophilic reactivity of 5 in Diels-Alder reactions has already been reported by several laboratories.^{18,19} The substrates investigated were open chain dienes, cyclopentadiene, cyclohexadiene, and anthracene. The latter gave a mixture of the meso and racemic adducts, likely derived by partial isomerization of 5 into 6 at the temperatures required by the reaction.

Repetition of the reported work gave comparable results. Quite good results were also obtained in the reaction with several other dienes studied in order to define the limitation and potentiality of 5.

The experimental data for the cycloadducts 7a-11a are summarized in Table I. It should be noted that reaction conditions are relatively mild and that cis-trans isomerization of 5 into 6 is promoted at higher temperatures.

The ¹H and ¹³C NMR spectral data are collected in Table II (supplementary material).

Besides the correct elemental composition determined by combustion analyses, the ¹H and ¹³C magnetic parameters and the measurement of NOE enhancements in more controversial cases were essential for the assignment of the structures.

The ¹H resonances of bridgehead protons and of protons α to the sulfonyl groups are often well resolved multiplets and are particularly helpful for the structure elucidation. The C_s symmetry is shown by the limited number of resonances in the aliphatic region, while the aromatic portion, which is not diagnostic, is composed of two multiplets in the region between δ 7.43-7.74 and 7.98-8.02. The vinylic protons, when present, show the typical pattern of similar adducts in the expected region (δ 6.06-6.61). On the basis of simple acidity considerations and as a result of decou-

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Table III. Percent NOE Enhancements of Nonaromatic Resonances in Adducts 10, 11, 26, and 26'^a

10				11				26				26'	
A	B	{A}B	A{B}	A	B	{A}B	A{B}	A	B	{A}B	A{B}	{A}B	A{B}
1 (7)	2 (3)	5.7	5.2	1 (6)	2 (5)	5.1	4.8	1	3	0	0	0	0
	4	0	0.9		3 (4)	2.1	3.3		3'	0	0	0	0
	5	1.7	5.3		7 (8)	6.7	5.7		4	c	c	0	0
	6	7.5	7.7		9	3.8	4.3		5	c	c	0	0
	8 (9)	4.3	5.3		9'	3.8	2.9		6	13.7	13.3	13.3	13.1
2 (3)	4	9.8	9.5	2 (5)	3 (4)	1.7	2.2	3	3'	35.6	33.5	38.1	37.5
	5	0	0		7 (8)	3.4	2.4		4	5.0	3.3	7.1	4.2
	6	0	0		9	0	0		5	0	0	-2.5 ^e	-1.8 ^e
	8 (9)	5.0	7.3		9'	0	0		6	0	0	0	0
4	5	1.7	10.0	3 (4)	7 (8)	0	0	3'	4	4.8	3.3	4.3	3.0
	6	0	0		9	-3.0 ^b	-2.4 ^b		5	0	0	8.3	5.3
	8 (9)	0	0		9'	9.9	7.8		6	3.3	2.7	0	0
5	6	12.5	2.1	7 (8)	9	0	0.7	4	5	c	c	6.7	7.4
	8 (9)	0	0		9'	0	0		6	0	0	c	c
6	8 (9)	0	0	9	9'	31.1	33.4	5	6	7.7 ^d	3.3	4.0	3.8

^a Errors are estimated to be not greater than 2%. ^b Negative enhancement due to the quasilinearity of 3 (4), 9', and 9 protons. ^c Not measurable because of the proximity of the corresponding resonances. ^d Enhancement caused by perturbation of H₁ proton. ^e Negative enhancement due to the quasilinearity of 3, 3', and 5 protons.

Table IV. Reaction Conditions, Yields, and Physical Constants for the Cycloadducts Derived from (E)-1,2-Bis(phenylsulfonyl)ethylene (6)

cyclo-adduct	solvent	temp, °C	t, h	yield, %	mp, ^a °C	recrystallization solvent	microanalysis C, H found (calcd)
7b	CH ₂ Cl ₂	25	1	98	153 ^b	EtOEt	
8b	toluene	111	1	97	151 ^c	EtOEt	62.17 (61.83), 5.07 (5.19)
9b	toluene	111	15	92	176-177	CH ₂ Cl ₂ /EtOEt	62.90 (62.97), 4.83 (5.03)
22	CH ₂ Cl ₂	25	48	94	216-226	CH ₂ Cl ₂	57.15 (57.43), 4.26 (4.28)
23	toluene	111	48	77	141-142	CH ₂ Cl ₂ /EtOEt	62.86 (62.66), 5.42 (5.51)
24	<i>o</i> -DCB ^d	160	12	84	155-156	EtOEt	64.23 (64.05), 4.60 (4.89)
25	<i>o</i> -DCB ^d	160	14	22	87-88	EtOEt	65.17 (65.07), 4.99 (4.75)
26				38	91-92	EtOH	63.83 (63.69), 4.76 (4.45)
26'	neat	170	20	41	239	CH ₂ Cl ₂ /EtOEt	63.55 (63.69), 4.40 (4.45)
30	toluene	111	12	90	125-126	EtOEt	64.96 (64.83), 6.22 (6.35)
32b	neat	170	24	89	216	CH ₂ Cl ₂ /EtOEt	69.51 (69.11), 4.54 (4.56)

^a With partial decomposition. ^b Lit.³⁷ mp 257-259 °C (C₆H₆/EtOH). ^c Lit.^{19b} mp 153-154 °C (EtOH). ^d *o*-Dichlorobenzene.

pling experiments we assign the absorptions at fields immediately higher than the olefinic region to the protons α to the sulfonyl groups.

Also the resonances of the bridgehead carbons in the ¹³C NMR spectrum exhibit characteristic doublets in the δ 32-48 range, while those adjacent to the sulfonyl groups are doublets in the δ 70.0-71.5 range. Vinylic carbon resonances are located in the aromatic region together with those of the phenyl groups (δ 127-142 range).

Concerning the stereochemistry of the addition of (Z)-ethylene 5 to the cyclic dienes, we observed that the usual endo selectivity found in the addition of carbonyl-substituted olefins (Alder rule), due to the well-known secondary orbital interactions, is followed in many cases. Indeed the set of coupling constants in the proton NMR spectra is in agreement with the endo assignment (cycloadducts 7a-9a).

However an exception was encountered in the stereochemical assignment of the adduct 10. In fact in this case the protons α to the sulfonyl groups, H₈ and H₉, resonate as a singlet at 4.01 ppm, which shows no measurable coupling with the vicinal H₁ or H₇ protons. This fact is more in agreement with the exo configuration, where the dihedral angle between H₇ and H₈ (or H₁ and H₉) is close to 90°, than with the endo configuration. This assignment is corroborated by the measurement of NOE enhancements (the results are reported in Table III). No enhancement is observed between the H₆ and the H₈ (H₉) protons. On the other hand the latter give a measurable enhancement with the bridgehead H₁ (H₇) protons, thus

confirming the exo configuration.

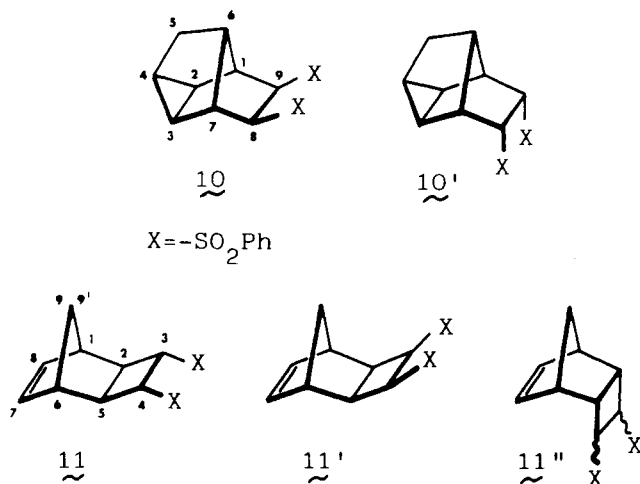
The exo mode of addition of the (Z)-ethylene 5 to norbornadiene is different from that observed for the addition of other dienophiles²⁰ which, as can be anticipated by the consideration of secondary orbital interactions, proceeds to give mostly the endo adducts. It is reasonable to suppose that in our case steric effects predominate over the electronic control in directing the stereoselectivity.

Similar ¹H NMR considerations have led to the assignment of structure 11 to the adduct of 5 and quadricyclane.²¹ In fact, of the four possible structures shown, the endo structures 11'' can be excluded in view of the well-established stereochemistry for the addition of other dienophiles and of the nature of the diene obtained from reductive elimination of the sulfonyl groups (see below). As for the exo structures 11 and 11', the coupling constant between H₂ and H₃ (or H₄ and H₅), which is less than 1 Hz, suggests the exo,endo structure 11 where, as shown by Dreiding models, the dihedral angle between these protons is close to 90°, whereas a dihedral angle of ca. 120° is found for the exo,exo isomer 11'.

Also in this case a more definite answer is given by NOE measurements (cf. Table III). Particularly revealing is the negative and positive enhancements found for H₉ and H_{9'}, respectively, upon perturbation of H₃ (H₄) or for H₃ (H₄) and H_{9'}, respectively, upon perturbation of H₉. These

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findings indicate the proximity of the H₃ and H₄ protons to H₉' and a quasilinear arrangement of H₉, H₉', and H₃ (H₄), H₉' being in the central position. Of the four potential adducts for 11, such an arrangement is found only in the exo,endo isomer 11.

As the stereochemistry for the addition to quadricyclane is similar to that found with other dienophiles, the anomalous stereochemistry observed for the addition to norbornadiene is actually to be attributed to steric factors. In conclusion the stereochemistry for the addition of 5 is governed by secondary orbital interactions but to a lesser extent than in the case of carbonyl-activated dienophiles. Steric effects may sometimes become predominant in directing the stereoselectivity.

The reactivity of 5 toward cyclic dienes is such that it may be classified among the rather reactive dienophiles. Indeed, in the series of cyclic penta-, hexa-, and heptadienes, where the reactivity decreases with the ring size because of decreasing ring strain and/or coplanarity of the 4π system, 5 reacts up to cyclohexadiene but not with the last one.

However 1,3-cycloheptadiene and other less reactive dienes, which resisted the attack of (*Z*)-ethylene 5, underwent successful addition with the more powerful (*E*)-1,2-bis(phenylsulfonyl)ethylene (6). Some examples are discussed in the next section.

Cycloaddition Reactions of (*E*)-1,2-Bis(phenylsulfonyl)ethylene (6). The experimental data for the new cycloadducts 9b, 22-26, and 30 are summarized in Table IV. For sake of completeness, the table also reports physical data and NMR spectral parameters for the already known adducts 7b, 8b, and 32b.

The analysis of the proton NMR spectra, though more complex than in the case of the isomeric *Z* adducts due to the absence of any molecular symmetry, is often straightforward. In fact, the nonaromatic absorptions, which appear as complex multiplets at 60 MHz, are separated in the 200-MHz spectra. Their assignment is assured by consideration of the coupling constants and by decoupling experiments. As a general trend the sequence of resonances from low to high fields is olefinic, α to sulfonyl, bridgehead, and aliphatic hydrogens. The same trend is assumed in the ¹³C spectra. Because the assignment is difficult and ambiguous, we do not report the carbon phenyl resonances in Table V (supplementary material).

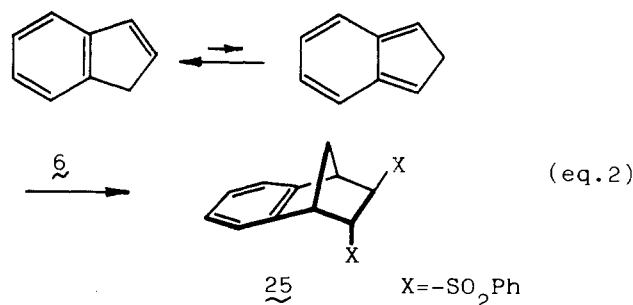
It is interesting to note that the solubility behavior during these cycloadditions is the opposite to that observed in the case of the (*Z*)-ethylene 5. In fact, while the (*E*)-ethylene 6 is sparingly soluble in the solvents used, the adducts are much more soluble, so that the completion of

the reaction is easily monitored by the disappearance of any precipitate in the reaction mixture. The opposite was generally observed with the *Z* isomer.

Though evident by the data reported in Table IV, the reactivity of 6 deserves some comments. The Diels-Alder addition to furane was reported not to occur in benzene even under reflux. When carried out in chlorinated solvents, such as chloroform or methylene chloride, the reaction is instead very facile and produces 22 in quantitative yields. The reason for this discrepancy with the literature may be due to the change in the reaction conditions and to the insolubility of this particular adduct in chlorinated solvents. Probably in other solvents the retro Diels-Alder process is thermodynamically favored.

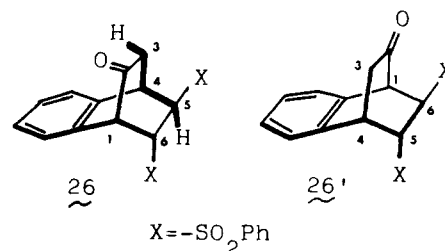
The different reactivity of 5 and 6 is shown by the smooth reaction of 6 with 1,3-cycloheptadiene (18) and cyclooctatetraene (COT) (19), whereas 5 does not react.²² In the case of COT a second adduct, probably derived by cycloaddition to the dimeric forms of COT, is also produced in variable amounts depending upon the reaction conditions. To avoid this side reaction a minimum excess of COT and a special procedure, described in the Experimental Section, has to be used.

Indene reacts with 6 to afford the benzonorbornene adduct 25 albeit in low yields. The mechanism is probably as illustrated in eq 2 with the intermediacy of isoindene,



formed by an allowed 1,5-suprafacial sigmatropic shift. The only precedent to this reaction is presented by the addition of maleic anhydride.²³

The reaction of 6 with β-naphthol produces in good yield a mixture of two products, 26 and 26', that were separated



by silica gel column chromatography.

The ¹H NMR spectroscopic analysis of the stereochemistry of the two adducts is not straightforward; however a reasonable hypothesis of their structures as indicated in 26 and 26' may be formulated. Of some diagnostic value is the inspection of methylenic resonances. They give rise to an AB system, further split because of coupling with the bridgehead protons. The high-field part of the system is to be attributed to the proton syn to the benzene ring

(22) The only product isolated from the reaction of 5 with COT (19) was a cycloadduct with dimeric forms of COT but whose structure could not be exactly assigned because it was insoluble in the most common solvents.

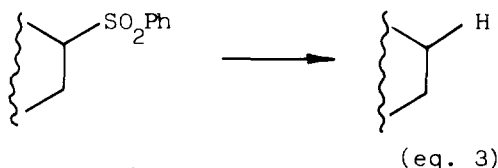
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because of the shielding effect of the aromatic electronic anisotropy. This multiplet is a doublet of doublets (at δ 2.40) in the isomer which elutes later (mp 239 °C) but shows a further splitting (at δ 2.21) in the isomer eluted earlier (mp 91–92 °C). It is reasonable to attribute the splitting to a coupling with H_5 in structure 26, which is the only proton α to a sulfonyl in a W arrangement. This assignment is substantiated by decoupling experiments.

Further support of the assignment is provided by NOE measurements. The perturbation of the low-field part of the AB methylenic system (at 3.32 and 2.72 ppm respectively for 26 and 26') induces a 3.0 and 6.8 enhancement of H_5 in the first and second eluted isomers, respectively. These findings are in accordance with the proposed structures as judged from examination of Dreiding models.

As a final point, the ene reaction of β -pinene is an additional example of the broad range of applications of 6. The 1H and ^{13}C spectra of the resulting cycloadduct 30 are well in agreement with those obtained by cycloaddition of other dienophiles.²⁴ The proposed structure is confirmed by the reductive desulfonylation to the hydrocarbon 31. Note that α -pinene does not react with 6 under the employed conditions; to the best of our knowledge no enophilic reactions of α -pinene with C=C dienophiles have been reported, even with maleic anhydride.

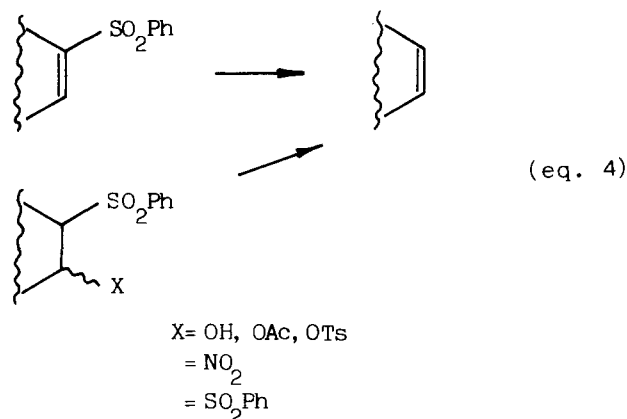
Reductive Desulfonylation of 1,2-Bis(phenylsulfonyl)ethanes. It is a known, well-established synthetic procedure that sulfones can be reductively desulfonylated to the corresponding alkane. For example various metal amalgams^{25a} or other reducing agents^{25b} can mediate the transformation shown in eq. 3.



In a similar way, unsaturated sulfones can be transformed into alkenes by treatment with sodium amalgam in methanol,²⁶ potassium graphite,²⁷ Grignard reagents in the presence of nickel salts,²⁸ or sodium dithionite.²⁹

On the other hand, carbon-carbon double bond formation is reported to occur on reductive treatment of β -halogeno, hydroxy, acetate, or tosylate sulfones³⁰ with a variety of reagents or of β -nitro sulfones³¹ with tri-*n*-butyltin hydride. To the best of our knowledge, however, no examples have so far been reported on carbon-carbon double bond formation from β -disulfonyl ethanes. Indeed, sodium amalgam reduction of the cycloadducts derived by cycloaddition of either (Z)- or (E)-1,2-bis(phenylsulfonyl)ethylenes (5 and 6) in methanol buffered with

sodium dihydrogen phosphate did afford the desired carbon-carbon double bond in good to excellent yields.

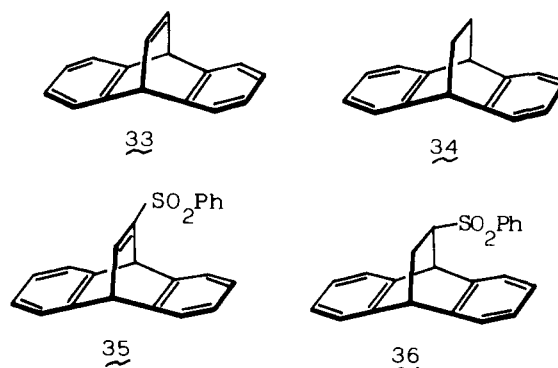


On the basis of the general procedure described in the Experimental Section, the formation of the following hydrocarbons was easily accomplished starting from the Z cycloadducts 7a–11: norbornadiene (12), 65%; bicyclo[2.2.2]octa-2,5-diene (13), 69%; tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (14), 60%; tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (deltacyclene) (15), 58%; tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (16), 59% yield. Of particular interest is the easy two-step preparation of 16, that has no comparable routes of synthesis as far as yields and simplicity of operations are concerned.

Also the adducts derived from the cycloaddition of the E-ethylene 6 undergo reductive desulfonylation under the same conditions. Bicyclo[3.2.2]nona-6,8-diene (27) was obtained in 84% yield and tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (Nenitzescu hydrocarbon) (28) in 75% yield.

The reported yields refer to isolated products. They have not been fully optimized and particularly for volatile products they are affected by losses in the workup.

A preliminary study on the reductive elimination reaction, particularly from the point of view of yields and alternative reducing agents, was carried out on the adduct of 6 with anthracene 32b as the product; 2,3,5,6-dibenzobicyclo[2.2.2]octa-2,5,7-diene (dibenzobarralene) (33) is not volatile, due to its high molecular weight, under the workup conditions. Synthetically useful yields were obtained with the previously described procedure, i.e., sodium amalgam in methanol buffered with NaH₂PO₄·H₂O as well as with sodium in refluxing toluene or with lithium amalgam in toluene. Concerning the first procedure, which was adopted as a general method for the reduction of the other adducts because of its simplicity and mildness, the effect of the buffer is critical. In fact, experiments in which no buffer or other salts were used gave erratic results and a mixture of products, among which the unsaturated compound 32, the vinylic sulfone 35, and the saturated analogues 34 and 36 were detected (see Experimental Section).



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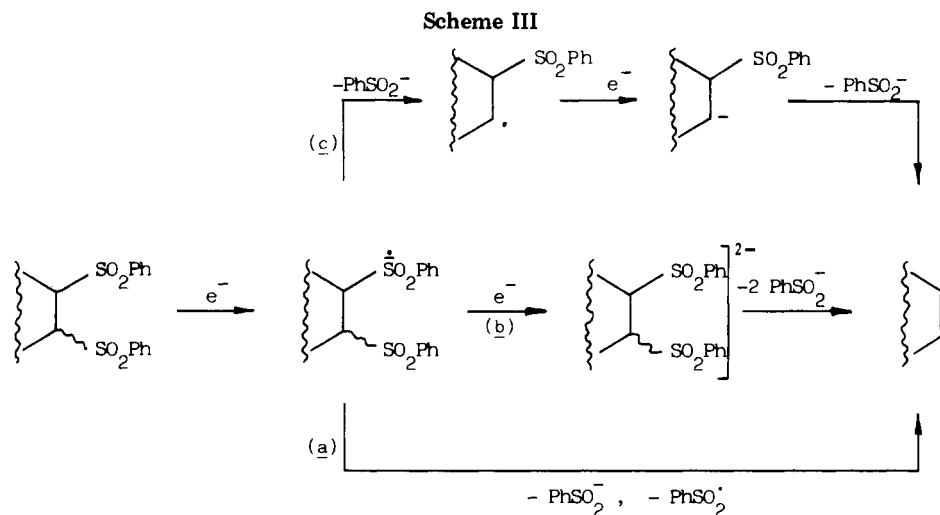
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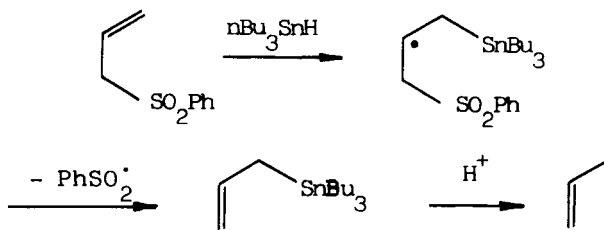
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The reduction mediated by lithium amalgam in methanol, lithium in toluene, sodium in ether, aluminium amalgam in tetrahydrofuran–water,³² tri-*n*-butyltin hydride in benzene,³¹ and sodium iodide in acetone³³ proved to be ineffective, giving back starting material as the only isolable product. A mixture of unidentified products were obtained by LiAlH₄ reduction in ether, sodium sulfide in dimethylformamide,³³ and lithium or sodium in ethylamine.³⁰

Concerning the mechanism of desulfonylation, we believe the key step involves electron transfer from the metal to the sulfonyl group. The generated radical anion may (a) expel a molecule of PhSO₂⁻ and one of PhSO₂[•], (b) be further reduced to produce a molecule of the olefin and two molecules of PhSO₂⁻, or (c) lose the two PhSO₂⁻ fragments one at a time with the intermediate reduction of the neutral radical as illustrated in Scheme III.

These processes are supported by related precedents in the literature. For example the one electron transfer mechanism is supported by the work of Shevlin and co-workers.³⁴ They showed that when a radical is generated β to a sulfonyl group by *n*-Bu₃SnH reduction of β-halogeno sulfones, it expels PhSO₂[•] to afford olefins in good yields. Nitrosulfones are similarly eliminated.³¹ Finally, the work by Ueno³⁵ has shown that allylic sulfones are desulfonylated in a related mechanism, illustrated in eq 5.



(eq. 5)

Preliminary electrochemical results suggest a two-electron transfer mechanism for the desulfonylation of **32b** but more work is necessary to provide a more definite answer on the mechanism of the process, even though the pro-

posed mechanism is widely supported by the electrochemical reduction of β-halogeno sulfones.³⁶

Experimental Section

Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker WP 200 operating at 200.13 or 50.30 MHz, respectively. Alternatively a Varian EM 360A or a Bruker WP 60, both operating at 60 MHz, were used. Microanalysis were performed by G. Biasioli of Prof. E. Celon's Laboratorio di Microanalisi staff. Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data. The yields, spectral data, and physical constants of all new compounds are collected in the tables.

(Z)-1,2-Bis(phenylsulfonyl)ethylene (5). Compound **5** was prepared in ca. 80% overall yield by the reported procedure:^{17,37} mp 100–101 °C (ether) (lit.¹⁷ mp 99–100 °C, lit.³⁷ 89.5–90 °C); ¹H NMR (CDCl₃, Me₄Si) δ 6.82 (2 H, s), 7.54–7.76, 8.08 (10 H, C₆H₅, m); ¹³C NMR (CDCl₃, Me₄Si) δ 128.75 (d, Ph), 129.41 (d, Ph), 134.49 (d, Ph), 139.91 (s, Ph), 140.66 (d).

(E)-1,2-Bis(phenylsulfonyl)ethylene (6). **Method A.** (Z)-1,2-Bis(phenylthio)ethylene (81.0 g, 0.33 mol) was placed into a 100-mL round-bottomed flask and flame distilled at 14 torr; a single fraction was collected between 220–230 °C. The distillate (70.1 g, 87% yield) slowly solidifies on standing and contains a mixture of the two isomers in the approximate ratio *E*:*Z* = 8:2. The mixture of isomers was directly submitted to oxidation. Thus, 70.1 g (0.29 mol) of the mixture was placed into a 2-L, three-necked, round-bottomed flask equipped with magnetic spinbar, dropping funnel, and reflux condenser and dissolved in ca. 700 mL of glacial acetic acid. While stirring at 0 °C, 200 mL of 36% H₂O₂ and few drops of concentrated H₂SO₄ were added dropwise over 15 min. The ice bath was removed and replaced with an oil bath that was heated to ca. 120 °C. After 3 h, the colorless reaction mixture was cooled and the white crystals of (*E*)-1,2-bis(phenylsulfonyl)ethylene (**6**) were filtered off, 55.16 g (62% yield). The mother liquors were treated with Na₂S₂O₅ to reduce the excess of oxidant and the solvent was removed (50 °C, 14 torr) affording a colorless oil to which was added excess saturated aqueous Na₂CO₃ until the evolution of CO₂ had ceased. CH₂Cl₂ (ca. 30 mL) was added and the aqueous phase was extracted with more CH₂Cl₂ (2 × ca. 30 mL), washed with brine and water, and rot-evaporated (30 °C, 14 torr). The oily residue of (Z)-1,2-bis(phenylsulfonyl)ethylene (**5**) was crystallized with ether affording bright, colorless plates, 20.35 g (23% yield).

Method B. To a solution of 50 g (0.16 mol) of (Z)-1,2-bis(phenylsulfonyl)ethylene (**5**) in 100 mL of CH₂Cl₂ was added several crystals of iodine producing a homogeneous violet solution.

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Irradiation at 300 nm in a Rayonet photoreactor or exposure to sun light afforded a white precipitate. When the absence of the Z isomer was observed (TLC, CH₂Cl₂ eluant, UV detection) the solid was filtered off and washed with a small amount of CH₂Cl₂, 44 g (88% yield). It may be recrystallized from CH₃CN: mp 219.5 °C (lit.¹⁷ 226–229 °C); ¹H NMR (CDCl₃, Me₄Si) δ 7.37 (2 H, s), 7.57–7.80, 7.91 (10 H, C₆H₅, m); ¹³C NMR (CDCl₃, Me₄Si) δ 128.55 (d, Ph), 129.90 (d, Ph), 134.85 (d, Ph), 138.25 (s, Ph), 140.67 (d).

A. Cycloadducts from (Z)-1,2-Bis(phenylsulfonyl)ethylene (5). *endo*-2,3-Bis(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (7a). To a solution of 0.5 g (1.6 mmol) of (Z)-1,2-bis(phenylsulfonyl)ethylene (5) in 5 mL of CH₂Cl₂ contained in a 25-mL round-bottomed flask was added freshly distilled cyclopentadiene (0.5 g, 2.2 mmol) and the solution swirled to homogeneity. On standing white crystals separated, 0.6 g (98% yield).

endo-2,3-Bis(phenylsulfonyl)bicyclo[2.2.2]oct-5-ene (8a). A 10-mL, screw-capped, heavy-walled Pyrex test tube was charged with freshly distilled 1,3-cyclohexadiene (0.3 g, 3.7 mmol) and (Z)-1,2-bis(phenylsulfonyl)ethylene (5) (1.0 g, 3.7 mmol) in 2 mL of toluene. The test tube was sealed and immersed into an oil bath preheated at 120–130 °C. The reaction mixture soon became homogeneous and after some time a white solid separated. After stirring at this temperature overnight the reaction mixture was cooled and a little ether added to complete the precipitation. The solid was filtered with suction and washed with more ether. A white, crystalline solid was obtained, 1.15 g (91% yield).

anti-6,7-Bis(phenylsulfonyl)tricyclo[3.2.2.0^{2,4}]non-8-ene (9a). The procedure described for 8a was followed. Thus 1.0 g (3.2 mmol) of 5 and 0.5 g (5.4 mmol) of cycloheptatriene in 2 mL of toluene afforded 1.2 g (92% yield) of 9a.

8,9-Bis(phenylsulfonyl)tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (10a). The procedure described for 8a was employed.^{14b}

3,4-Bis(phenylsulfonyl)tricyclo[4.2.1.0^{2,5}]non-7-ene (11a). The procedure described for 7a was employed.^{14b}

meso-1,2-Bis(phenylsulfonyl)-9,10-ethanoanthracene (32a). The described procedure¹⁸ was employed with the following modifications. A 25-mL, screw-capped vial was charged with (Z)-1,2-bis(phenylsulfonyl)ethylene (5) (3 g, 9.73 mmol) and anthracene (2.0 g, 11.22 mmol). The solid mixture was heated with stirring at 180 °C in an oil bath for 18 h. The black molten mixture was then cooled and chromatographed on a short silica gel (70–230 mesh) column (ca. 8:1 weight ratio adsorbant to substrate) eluting with a gradient CH₂Cl₂/EtOEt mixture to afford three products which were pure by TLC (silica gel, eluant CH₂Cl₂, UV detection). The first eluate was the excess anthracene, the second the racemic cycloadduct 32b (2.22 g, 47% yield) derived by the partial isomerization of the dienophile under the reaction conditions. The third eluate was the *meso* cycloadduct 32a, 2.16 g (46% yield).

B. Cycloadducts from (E)-1,2-Bis(phenylsulfonyl)ethylene (6). *2-exo,3-endo*-Bis(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (7b). A mixture of 0.5 g (1.6 mmol) of (E)-1,2-bis(phenylsulfonyl)ethylene (6) and 0.15 g (2.2 mmol) of cyclopentadiene in 5 mL of reagent grade CH₂Cl₂ were swirled occasionally for 1 h until fully dissolved. The solvent was partially rotoevaporated (30 °C, 14 torr) and ether was added. On cooling white crystals precipitated which were removed by suction filtration and air dried, 0.6 g (98% yield).

2-exo,3-endo-Bis(phenylsulfonyl)bicyclo[2.2.2]oct-5-ene (8b). A sample of 6 (0.5 g, 1.6 mmol) and 1,3-cyclohexadiene (0.25 g, 3.12 mmol) in 1.5 mL of toluene was prepared in a screw-capped vial and heated at 120 °C in an oil bath for 60 min. The solution became homogeneous and remained in this state on cooling to room temperature. Most of the solvent was stripped off from the pale yellow solution (60 °C, 14 torr) and ether added. The white precipitate was suction filtered, washed with a little cold ether, and dried, 1.1 g (97% yield).

6-exo,7-endo-Bis(phenylsulfonyl)tricyclo[3.2.2.0^{2,4}]non-8-ene (9b). The procedure described for 8a was employed. Thus a mixture of 1.0 g (3.2 mmol) of 6 and 0.5 g (5.4 mmol) of cycloheptatriene afforded 1.2 g (92% yield) of a white, crystalline solid.

7-Oxa-2-*exo,3-endo*-bis(phenylsulfonyl)bicyclo[2.2.1]hept-5-ene (22). To 2.0 g (6.4 mmol) of (E)-1,2-bis(phenylsulfonyl)ethylene (6) partially dissolved in CH₂Cl₂ (ca. 30 mL) was added 1.2 g (17.6 mmol) of furan while stirring. The white

suspension was stirred at room temperature for 6–7 h until all the solid had dissolved and the reaction mixture was transparent and colorless. Stirring was discontinued, the stirring bar was removed, and the solution was allowed to stand overnight. Ether was added to complete the precipitation and the white solid was filtered, washed with ether, and dried, 2.3 g (94% yield).

5-exo,6-endo-Bis(phenylsulfonyl)bicyclo[3.2.2]non-7-ene (23). A screw-capped, heavy-walled, Pyrex test tube was charged with 0.5 g (1.6 mmol) of 6 and 0.35 g (3.7 mmol) of 1,3-cycloheptadiene in 2 mL of toluene. The reaction mixture was heated with stirring for 48 h at 150 °C to afford a brown homogeneous solution which was stripped of solvent by rotoevaporation (ca. 60 °C, 14 torr); the residue was chromatographed through 70–230 mesh silica gel (ca. 10:1 weight ratio adsorbant to substrate) eluting with CH₂Cl₂. The product crystallized by slow addition of ether to a concentrated solution of 23 in CH₂Cl₂, 0.5 g (77% yield).

5-exo,6-endo-Bis(phenylsulfonyl)tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (24). A screw-capped, 10-mL test tube was charged with 0.5 g (1.6 mmol) of 6 and 1.5 mL of *o*-dichlorobenzene and a small magnetic spinbar. The test tube was immersed into an oil bath preheated at 170 °C until all the solid had dissolved and cyclooctatetraene (0.25 mL, 2.2 mmol) was added. After sealing the reaction mixture was heated, while stirring, at 170 °C overnight. The completion of the reaction was signaled by cooling; when no more solid material precipitated the thick, pale yellow, oily product was distilled free (Kugelrohr) of the dichlorobenzene and the residue was chromatographed on 70–230 mesh silica gel (ca. 10:1 weight ratio adsorbant to substrate) eluting with a gradient of petroleum ether/CH₂Cl₂. The product crystallized on adding ether to a concentrated CH₂Cl₂ solution, 0.56 g (84% yield).

2-exo,3-endo-Bis(phenylsulfonyl)-5,6-benzobicyclo[2.2.1]hept-5-ene (25). A 10-mL, screw-capped test tube containing 1.0 g (3.2 mmol) of 6 and 0.6 g (5.2 mmol) of indene was purged for several minutes with a flow of argon, closed, and immersed into a preheated oil bath at ca. 160 °C for 14 h. After cooling, the resulting black solid was chromatographed through silica gel (70–230 mesh, ca. 15:1 weight ratio adsorbant to substrate, eluant CH₂Cl₂). After a first fraction of hydrocarbons a slightly brown fraction containing the product was isolated. Several recrystallizations (CH₂Cl₂/EtOEt) gave colorless crystals, 0.15 g (22% yield).

2-Oxo-5-*exo,6-endo*- and 2-Oxo-5-*endo,6-exo*-bis(phenylsulfonyl)-7,8-benzobicyclo[2.2.2]oct-7-ene (26 and 26'). (E)-1,2-Bis(phenylsulfonyl)ethylene (6) (1.0 g, 3.2 mmol) and β-naphthol (1 g, 6.9 mmol) were stirred at 170 °C for 20 h. The resulting black reaction mixture was dissolved in CH₂Cl₂ and chromatographed (70–230 mesh silica gel, ca. 15:1 weight ratio adsorbant to substrate, eluant CH₂Cl₂). After a fraction containing the excess of β-naphthol, 26 was eluted as a colorless oil, which crystallized from EtOH, 0.55 g (38% yield). The eluant was replaced with a 9:1 mixture of CH₂Cl₂/EtOEt to elute 26' as colorless crystals that were recrystallized (CH₂Cl₂/EtOEt), 0.6 g (41% yield).

3-Pinenyl-1,2-bis(phenylsulfonyl)propane (30). Into a 25-mL, round-bottomed flask was placed 0.4 g (2.9 mmol) of β-pinene, 0.5 g (1.6 mmol) of 6, and 1.3 mL of toluene. The resulting reaction mixture was stirred at 150 °C overnight. The resulting clear yellow solution was rotoevaporated (60 °C, 14 torr) to a sticky solid which was crystallized from CH₂Cl₂/EtOEt affording colorless crystals, 0.65 g (90% yield).

Racemic 1,2-Bis(phenylsulfonyl)-9,10-ethanoanthracene (32b). (E)-1,2-bis(phenylsulfonyl)ethylene (6) (5.0 g, 16.2 mmol) and anthracene (3.2 g, 18.0 mmol) were heated at 160–180 °C for 24 h in a screw-capped vial. The resulting black material was dissolved in ca. 5 mL of CH₂Cl₂ and chromatographed through 70–230 mesh silica gel (ca. 10:1 weight ratio adsorbant to substrate, eluant CH₂Cl₂). After the first fraction (anthracene), the only other fraction was concentrated in vacuo, ether was added, and the crystals were filtered, washed with ether, and dried, 7.0 g (89% yield).

General Procedure for the Sodium Amalgam Reduction. A slurry of the bis(phenylsulfonyl)ethylene adduct (2.5 mmol) and ca. 6 g of NaH₂PO₄·H₂O in ca. 50 mL of methanol was purged with nitrogen gas. With efficient stirring sodium amalgam (2–6%, ca. an 8:1 equivalent ratio sodium to substrate) was added in

portions. The reaction mixture was kept stirring overnight at room temperature, then filtered, poured into brine, and extracted (3 × ca. 20 mL) with pentane. The extracts were washed with brine (3 × ca. 30 mL) and dried over anhydrous Na₂SO₄. Cautious rotoevaporation of the solvent (especially for volatile products) afforded the unsaturated adduct which was characterized by comparison with authentic samples or by matching the spectral data with those reported in the literature.

Bicyclo[2.2.1]hepta-2,5-diene (12). By the described procedure **7a** (1.0 g, 2.7 mmol) was converted into norbornadiene after cautious rotoevaporation of the solvent (0 °C, 20–25 torr) as a virtually pure (except for solvent traces) colorless oil (0.16 g, 65% yield) whose NMR parameters are identical with those reported.³⁸

Bicyclo[2.2.2]octa-2,6-diene (13). According to the general procedure described above, **13** was obtained, starting from 1.0 g (2.6 mmol) of **8a**, as a colorless semisolid (0.19 g, 69% yield) and identified by comparison of the ¹H NMR spectral parameters with those of an authentic sample.³⁹

Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (14). According to the procedure described above **14** was prepared, starting from 1.0 g (2.5 mmol) of **9a**, as a colorless semisolid (0.18 g, 61% yield) and characterized by the comparison of its ¹H NMR spectrum with that of an authentic sample.⁴⁰

Bicyclo[3.2.2]nona-6,8-diene (27). According to the general procedure described above, **27** was prepared, starting from 1.0 g (2.48 mmol) of **23a**, as a colorless wax (0.26 g, 84% yield) and was characterized by comparison of its ¹H NMR spectral data with those of an authentic sample.⁴¹

Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (28). From 1 g (2.4 mmol) of the precursor **24**, using the described general procedure, 0.23 g (74% yield) of Nenitzescu hydrocarbon **28** was obtained as a colorless semisolid and characterized by comparison of ¹H NMR spectral data with those of an authentic sample.⁴²

2-(2-Propenyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (1,4-Homonopadiene) (31). According to the described general procedure **31** was prepared from 0.3 g (0.68 mmol) of the β-pinene adduct **30** as a colorless oil: 0.11 g (93% yield); ¹H NMR (CDCl₃, Me₄Si) δ 0.82 (3 H, CH₃, s), 1.16 (1 H, H_{endo}, d, *J* = 8.54 Hz), 1.26 (3 H, CH₃, s), 1.96–2.16 (2 H, m), 2.22 (2 H, m), 2.35 (1 H, m), 2.70 (2 H, m), 4.96 (1 H, m), 5.03 (1 H, dm, *J*_d = 7.02 Hz), 5.23 (1 H, H₃, m), 5.63–5.86 (1 H, m); mass spectrum, *m/e* 162.

5,6:7,8-Dibenzobicyclo[2.2.2]octa-2,5,7-triene (33). (a) **With Sodium Amalgam in Methanol/NaH₂PO₄.** Dibenzobarralene (**33**) was prepared by the general procedure described with sodium

amalgam in MeOH buffered with NaH₂PO₄·H₂O, starting from 3.0 g (6.16 mmol) of the racemic isomer **32**, as a colorless solid (1.14 g, 91% yield, mp 118–119 °C (lit.¹⁰ 118.5–119 °C)) and was characterized by comparison of the ¹H NMR spectral data with those of an authentic sample.¹⁰

(b) **With Sodium in Toluene.** To a solution of **32b** (0.3 g, 0.62 mmol) in ca. 20 mL of toluene (freshly distilled from Na) was added Na (0.1 g, 4.3 mol) in small pieces and the reaction mixture was refluxed for 2 h. Water was cautiously added, the mixture was filtered into a separatory funnel, and the organic layer was washed twice with more water. Rotoevaporation of the solvent (20 °C, 14 torr) afforded a colorless solid (113 mg, 90% yield).

(c) **With Lithium Amalgam.** Cycloadduct **32b** (0.3 g, 0.62 mmol) in ca. 20 mL of dry toluene was treated with 1 g of 3% lithium amalgam (4.32 mol of Li) for 14 h at room temperature. Workup as before gave 0.12 g (95% yield) of **33**.

Reaction of 32b with Sodium Amalgam in MeOH (without Buffer). From the reaction of 0.5 g (1.03 mmol) of **32b** with 4% sodium amalgam in MeOH as previously described, a mixture of products was obtained which was separated by thick-layer chromatography (silica gel, eluant CH₂Cl₂). The first eluted material was ca. a 2:1 mixture of the saturated and unsaturated hydrocarbon **33** and **34** (0.18 g), while the second fraction was a mixture of the sulfones **35** and **36** (ca. 10 mg), characterized by comparison of the ¹H NMR spectral data with those of authentic material prepared as described.^{10,11,13} The estimated mass balance accounted for ca. 96% of products.

Reaction of 32b with Sodium Amalgam in MeOH/Na₂HPO₄. The same reaction conducted with from 0.5 g (1.03 mmol) of **32b**, 6 g of sodium amalgam, and Na₂HPO₄·12H₂O (ca. 2 g) suspended in MeOH afforded, as shown by ¹H NMR, a mixture of **33** and **34** (0.19 g) and traces of the sulfones **35** and **36** for an estimated mass balance of ca. 98% of products.

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Registry No. 5, 963-15-5; 6, 963-16-6; **7a**, 27770-83-8; **7b**, 88197-34-6; **8a**, 83818-43-3; **8b**, 88197-35-7; **9a**, 83818-44-4; **9b**, 88197-36-8; **10a**, 88197-32-4; **11a**, 88197-33-5; **12**, 121-46-0; **13**, 500-23-2; **14**, 7092-05-9; **22**, 87057-40-7; **23**, 87057-41-8; **24**, 87057-42-9; **25**, 87057-43-0; **26**, 87099-06-7; **26'**, 7164-08-1; **27**, 7164-08-1; **28**, 21604-76-2; **30**, 88132-62-1; **31**, 88132-64-3; **32a**, 88132-61-0; **32b**, 88132-63-2; **33**, 2734-13-6; **34**, 5675-64-9; **35**, 88132-65-4; **36**, 73301-18-5; (*Z*)-1,2-bis(phenylthio)ethylene, 18893-62-4; (*E*)-1,2-bis(phenylthio)ethylene, 18893-63-5; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; cycloheptatriene, 544-25-2; anthracene, 120-12-7; furan, 110-00-9; 1,3-cycloheptadiene, 4054-38-0; cyclooctatetraene, 629-20-9; indene, 95-13-6; β-naphthol, 135-19-3; β-pinene, 127-91-3.

Supplementary Material Available: Tables II and V, ¹H and ¹³C NMR spectral data for the cycloadducts derived from **5** and **6** (3 pages). Ordering information is given on any current masthead page.

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