Formation of Polysubstituted 1,2,5,6-Tetrahydropyridines from the 4 + 2 Cycloaddition Reaction of Bis(phenylsulfonyl)butadienes with Aryl Imines

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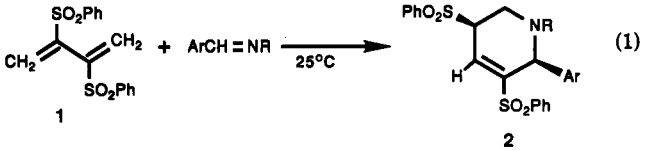
The reaction of 2,3-bis(phenylsulfonyl)-1,3-butadiene with aryl imines affords *N*-alkyl-3,5-bis(phenylsulfonyl)-1,2,5,6-tetrahydropyridines in high yield. The formation of the rearranged cycloadducts proceeds by a mechanism that involves addition of benzenesulfinate anion onto the terminal π-bond of the activated diene. The resulting carbanion undergoes proton transfer followed by aryl sulfinate ejection to give 1,3-bis(phenylsulfonyl)-1,3-butadiene as a transient intermediate. This reactive diene undergoes a rapid 4 + 2 cycloaddition followed by a subsequent hydrogen 1,3-shift. Support for the proposed mechanism is provided by the observation that a mixed cycloadduct is obtained from the reaction of a 1:1 mixture of 2,3-bis(phenylsulfonyl)- and 2,3-bis[(*o*-nitrophenyl)sulfonyl]butadiene with *N*-benzylidenemethylamine. An additional piece of supporting data for the proposed mechanism is the much shorter reaction time necessary for the reaction to go to completion when a small amount of sodium benzenesulfinate is added to the reaction mixture. 1,3-Bis(phenylsulfonyl)butadiene was independently synthesized by two different routes. This diene was found to rapidly react with a variety of imines to give the same cycloadducts as those derived from the 2,3-isomer. The reaction of several 4-substituted 1,3-bis(phenylsulfonyl)butadienes with aryl imines was found to give related 4 + 2 cycloadducts.

Multifunctional 1,3-dienes often exhibit high regio- and stereospecificity toward dienophiles, and consequently, these dienes are becoming well-established as useful intermediates in organic synthesis.[1-5] In particular, sulfur-substituted dienes have been widely used in cycloaddition reactions.[6] Compared to the all-carbon Diels–Alder reaction, the 4 + 2 cycloaddition of imines with sulfur-activated dienes has received only scant attention despite the enormous potential it holds for alkaloid synthesis.[7] Typically, imino Diels–Alder cycloadditions are successful only when the imine is activated in intramolecular cycloadditions[8-11] or involves the use of an iminium salt.[12-17] Our interest in this area was initiated by a study of the uncatalyzed Diels–Alder cycloaddition of 2,3-bis(phenylsulfonyl)-1,3-butadiene with various C–N π-bonds. Recent work in our laboratory has shown that the highly oxidized phenylsulfonyl dienes are versatile synthons that can be used for heterocyclic synthesis.[18] The phenylsulfonyl group is an extremely useful functionality in organic synthesis since it can enhance chemical reactivity and then can be easily removed to provide sulfur-free compounds.[19-21] In a preliminary report, we described our initial studies, which can be summarized in general terms by eq 1.[22] Thus, the reaction of 2,3-bis(phenylsulfonyl)-1,3-butadiene (1) with several *N*-alkyl aryl imines was found to give the novel rearranged cycloadduct 2 in high yield.



1 2 (1)

As an extension of our earlier work, we set out to investigate the scope, generality, and mechanistic details of this interesting transformation. In this paper, we report the result of these studies.

Results and Discussion

In spite of its simplicity and obvious potential as an activated diene, 2,3-bis(phenylsulfonyl)-1,3-butadiene (1) has not beeen extensively utilized for organic synthesis. This reagent was prepared in multigram quantities by a

Table I. Experimental Data for the X-ray Diffraction Study of 3,5-Bis(phenylsulfonyl)-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (3)

formula	$C_{24}H_{23}NO_4S_2$
FW	453.1
cryst syst	monoclinic
space gp	$P2_1/A$
a, Å	11.4322 (46)
b, Å	14.1993 (56)
c, Å	14.1748 (76)
β	108.964 (37)
V, Å	2176.09 (1.26)
Z	2
D_{calcd}, g/cm^3	1.38
diffractometer	Syntex P2
cryst size	0.25 × 0.38 × 0.18 mm
radiation	Mo Kα with graphite monochromator
scan speed	2.0–24.0 deg/min in 2θ
data collected	$+h,+k,\pm l$
scan type	coupled θ(crystal)–2θ(counter)
scan width	(Kα_1 − 1.0)–(Kα_2 + 1.1)
$2\theta_{max}$, deg	50.0
unique refl	3168
refl with $F^2 > 0$	2148
no. of variables	233
R_F	6.8%
R_{wF}	6.6%

† Dedicated with respect and admiration to Professor Michael P. Cava, one of the leading pioneers in the area of sulfone chemistry, on the occasion of his 65th birthday.

(1) Danishefsky, S. *Acc. Chem. Res.* **1981**, *14*, 400. Grayson, J. I.; Petrzilka, M. *Synthesis* **1981**, 7563; Hickmott, D. W. *Tetrahedron* **1984**, *40*, 2989.
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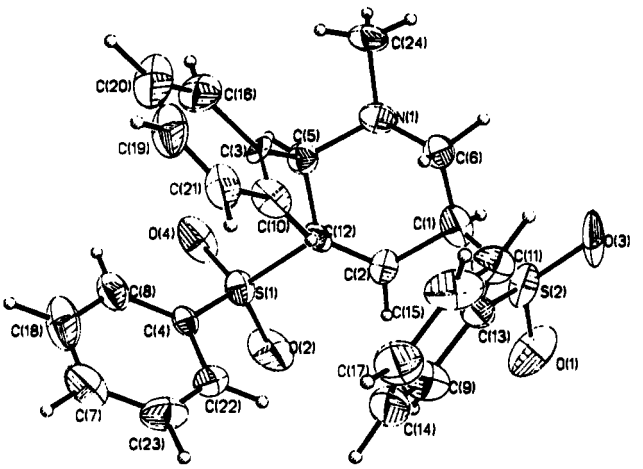
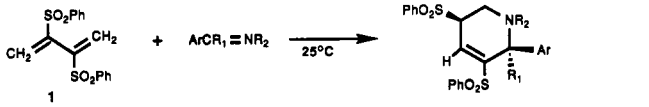


Figure 1. ORTEP drawing for 3,5-bis(phenylsulfonyl)-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (3).

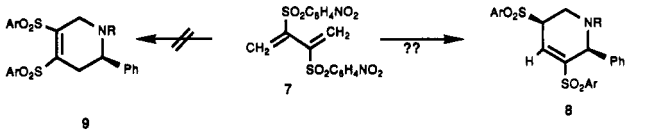
modification of the procedure of Okamura and Jeganathan.[23] As our first model, we investigated the Diels–Alder reaction of 1 with *N*-benzylidenemethylamine. A typical reaction was carried out by simply stirring the two reagents in methylene chloride at 25 °C for 24 h. The structure of the resulting rearranged cycloadduct 3 (90%) was assigned



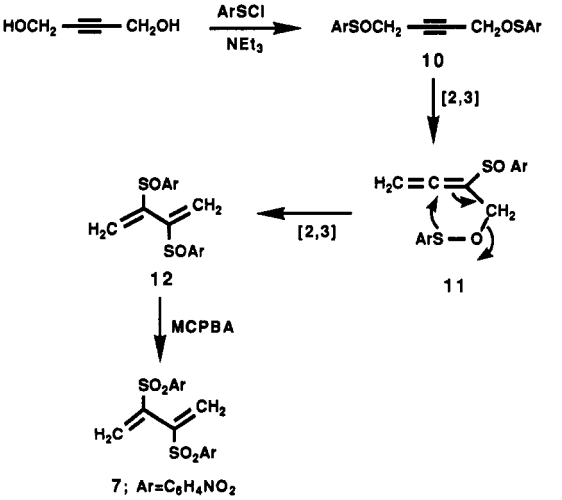
3; Ar=Ph; R_2=CH_3; R_1=H
4; Ar=Ph; R_2=CH_2Ph; R_1=H
5; Ar=Ph; R_2=CH_2Ph; R_1=D
6; Ar=α-naphthyl; R_2=CH_2Ph; R_1=H

on the basis of its characteristic spectral data and was further established by an X-ray single-crystal structure analysis. The crystallographic details can be found in Table I and the final ORTEP diagram in Figure 1. This surprising result warranted further studies of diene 1 with other imines so as to establish the generality of the process. Indeed, diene 1 reacts with several other imines under similar reaction conditions. In all cases, the cycloaddition afforded a single product corresponding to a rearranged cycloadduct. *N*-(1-Deuteriobenzylidene)benzylamine, when treated with diene 1, produced cycloadduct 5 where the deuterium was adjacent to the nitrogen atom. The cycloaddition did not occur with imines derived from aryl ketones.

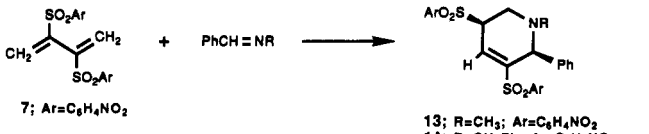
The imino group has been a relatively less utilized functionality in the synthesis of heterocyclic compounds. Certain derivatives of imines, however, have been previously employed in cycloaddition chemistry with heterosubstituted dienes, opening new opportunities for the construction of nitrogen heterocycles.[12] The successful use of heterosubstituted 1,3-dienes in synthesis demands knowledge of the substituent's effect on the cycloaddition rate, as well as the regio- and stereoselectivity of the process. Phenylsulfonyl substituents endow 1,3-dienes with useful Diels–Alder reactivity presumably because of their markedly lowered LUMO energy levels compared to 1,3-butadiene. Placement of a more potent electron-withdrawing substituent on the diene backbone might enable it to participate in Diels–Alder reactions with inverse electron demand. Thus, we became interested in determining whether the reaction of 2,3-bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (7) with various imines would lead to a rearranged cycloadduct or to the simpler 4 + 2 cycloadduct 9.



This diene was prepared by treating 2-butyne-1,4-diol with (*o*-nitrophenyl)sulfenyl chloride. The initially formed disulfenate ester 10 rapidly underwent a series of 2,3-sigmatropic rearrangements to give disulfoxide 12. This material was readily oxidized to 7 with MCPBA in excellent yield.



We have studied the reaction of 7 with two different aryl amines and found that the 3,5-bis(arylsulfonyl)-substituted tetrahydropyridine ring system (i.e., 13 or 14) was isolated as the exclusive product. None of the simple 4 + 2 cycloadduct was present in the crude reaction mixture.



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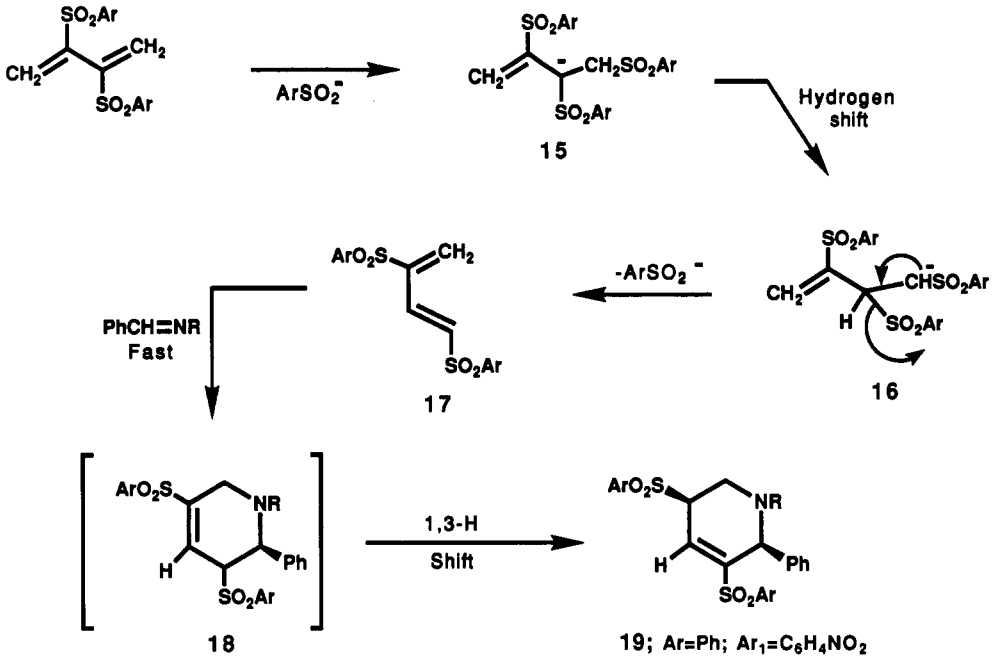
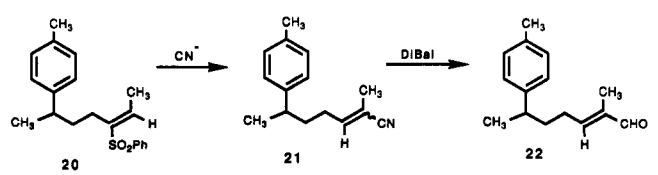
Scheme I



A mechanism that rationalizes the formation of the rearranged cycloadduct and is consistent with all the data (vide infra) is outlined in Scheme I. Carbanion **15** is a probable key intermediate in this novel sequence of reactions. Proton transfer from **15** generates anion **16**, which ejects the neighboring aryl sulfinate group to produce a 1,3-bis(arylsulfonyl)-substituted diene (i.e., **17**). This material undergoes a facile 4 + 2 cycloaddition with the added imine, and the resulting adduct **18** is transformed via a subsequent 1,3-hydrogen shift to the observed product. Presumably, a trace of aryl sulfinate anion was present in the reaction mixture and served as an initiator for the diene isomerization step. Supporting evidence for the proposed mechanism is provided by the observation that the reaction of a 1:1 mixture of dienes **1** and **7** afforded cycloadducts **3** and **13** as well as the mixed cycloadduct **19** in 25% yield. This is perfectly compatible with the reaction sequence outlined in Scheme I. An additional piece of supporting data for the proposed mechanism is the much shorter reaction time (ca. 2 h) necessary for the reaction to go to completion when a small amount of sodium benzenesulfinate is added to the mixture.

Credence is lent to the proposed addition–elimination sequence by a 1981 report by Taber and Saleh describing the synthesis of the sesquiterpene nuciferal (**22**).[24] The key step in the synthesis involved addition of cyanide to sulfone **20** followed by elimination of potassium arenesulfonate and conversion of the resulting nitrile **21** to nuciferal.[25]



At this stage of our studies, we decided to independently synthesize the 1,3-substituted diene **17** and establish its reactivity pattern. Some of the procedures currently available for the preparation of phenylsulfonyl-substituted 1,3-butadienes include (phenylsulfonyl)mercuration of 1,3-dienes,[26] condensation of allyl sulfones with aldehydes followed by acetylation and subsequent elimination,[27] thermal SO_2 extrusion from 2-(arylsulfonyl) sulfolenes,[28,29] cheletropic ring-opening of sulfolanes,[30] palladium(II)-catalyzed chloroacetoxylation of 1,3-dienes,[31] and the 2-tosylvinyl sulfone coupling with vinylstannanes.[32] Methods of preparing bis(phenylsulfonyl)-substituted 1,3-dienes, however, are limited to relatively few routes.[23,33-35] The first method we employed involved treating 1,3-bis(phenylsulfonyl)-1-propene (**23**)[35] with *n*-butyllithium followed by condensation with formaldehyde. In addition to the expected primary alcohol **24** (76%), diol **25** was also formed by the further reaction of **24** under the basic conditions used. We were unable to prevent formation of diol **25** even by altering the experimental conditions. Fortunately, the two products were easily separated by silica gel chromatography. Diol **25** was readily converted to 3,5-bis(phenylsulfonyl)-5,6-dihydro-2-pyran (**26**) upon treatment with a trace of acid or by chromatography on silica gel. Dehydration of the primary alcohol **24** was carried out by treatment with phosphorous tribromide followed by elimination with triethylamine.

(24) Taber, D. F.; Saleh, S. A. *J. Org. Chem.* **1981**, *46*, 4817.
(25) For some additional examples of related processes, see: Horner, L.; Hofer, W.; Ertel, I.; Kunz, H. *Chem. Ber.* **1970**, *103*, 2718. Padwa, A.; Yeske, P. *J. Am. Chem. Soc.* **1988**, *110*, 1617.
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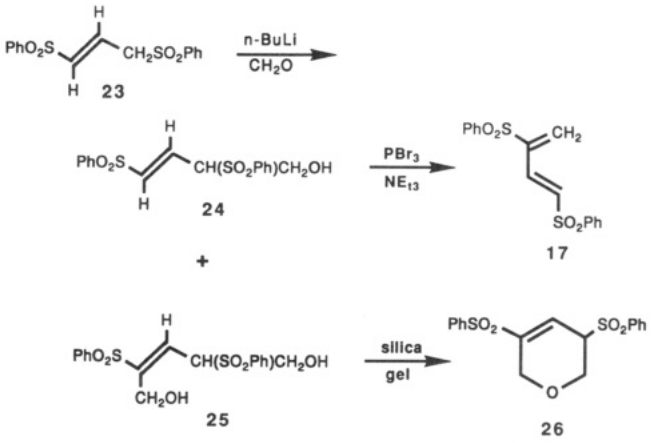
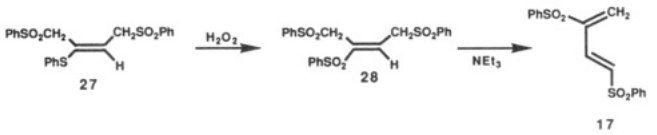
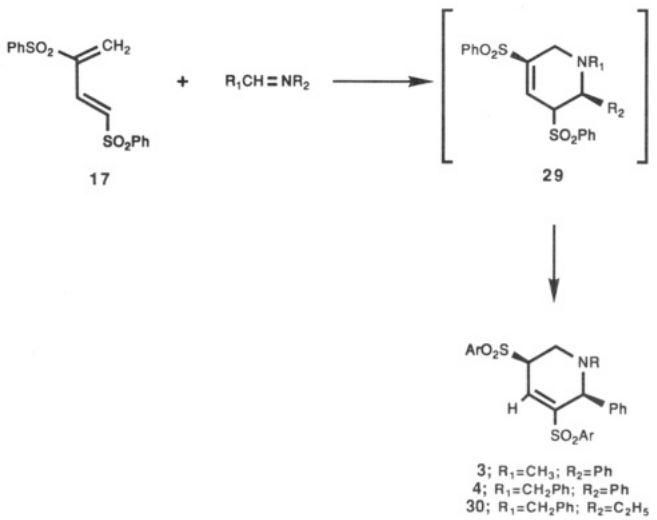
(36) Padwa, A.; Harrison, B.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1989**, *54*, 4232.



An alternate sequence that was also used to prepare diene **17** involved the oxidation of 1,4-bis(phenylsulfonyl)-2-(phenylthio)-2-butene (**27**)[34,35] to the corresponding sulfone **28** with a 30% hydrogen peroxide solution. Elimination of benzenesulfinate to give diene **17** was accomplished by stirring **28** with triethylamine in benzene at 25 °C.



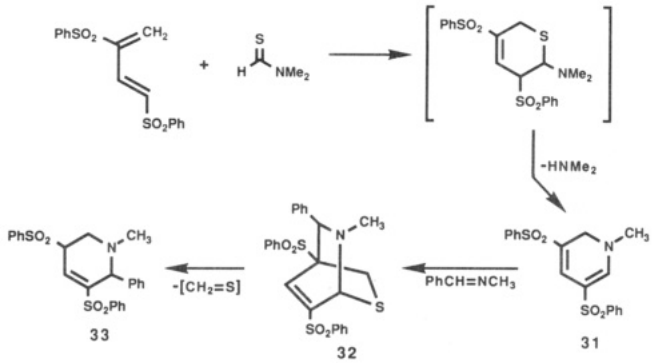
1,3-Bis(phenylsulfonyl)-1,3-butadiene (**17**) is highly activated toward nucleophilic addition as a consequence of its low LUMO energy. We examined the cycloaddition behavior of **17** and found that it readily reacts with the same imines that were used with the 2,3-diene. The reaction was over in less than 2 h at 25 °C and gave rise to the same cycloadducts that were obtained from the less reactive 2,3-isomer. Treatment of 1,3-bis(phenylsulfonyl)-1,3-butadiene (**17**) with an aliphatic imine (i.e., *N*-propylidenebenzylamine) produced the 4 + 2 cycloadduct **30** in 68% yield. All efforts to isolate cycloadduct **30** from the reaction of the 2,3-isomer, however, failed, and a complex mixture of products was obtained instead. All of our attempts to detect the rearranged 1,3-substituted diene **17** starting from the 2,3-bis(phenylsulfonyl)-substituted diene failed. This is undoubtedly related to the facility with which the 1,3-isomer reacts in the 4 + 2 cycloaddition process.[37]



(37) Attempts to detect diene **17** from **1** were also unsuccessful. Stirring for long periods of time led to uncharacterizable material.

Molecular mechanics calculations using the Still–Steliou program[38] were carried out, and the results indicated that the lowest energy conformer of the 1,3-isomer corresponds to the cisoid conformation necessary for the Diels–Alder reaction. The 2,3-substituted isomer, on the other hand, exists in the transoid form and possesses an enormous barrier (>50 kcal) for rotation about the 2,3-σ bond. MNDO calculations also indicate that 1,3-bis(phenylsulfonyl)-1,3-butadiene (**17**) is more highly activated toward cycloaddition as a consequence of its markedly lowered LUMO energy level (−1.39 eV) compared with the 2,3-substituted isomer (−0.29 eV).[39] The MM2 calculations also help rationalize the exclusive formation of the cis cycloadducts (**3**–**6**) and also account for the 1,3-hydrogen shift from *cis*-**29**. The calculations reveal a 3.2 kcal difference in steric energy between **3** (27.81 kcal) and **29** (R_1 = CH_3, R_2 = Ph, 31.01 kcal), which corresponds to the Diels–Alder cycloadduct derived from an endo transition state. The lower energy isomer corresponds to **3**, which presumably has fewer nonbonded interactions between the phenyl and phenylsulfonyl groups. The steric energy difference between **3** and the hypothetical trans cycloadduct **29** (*trans*-phenyl–phenylsulfonyl) groups (formed from an exo transition state) is also in favor of **3** by 1.8 kcal.

In an effort to extend the methodology to other heterodienophiles, we treated diene **17** with *N*,*N*-dimethylthioformamide and isolated 2*H*-thiopyran **31** in 78% yield.



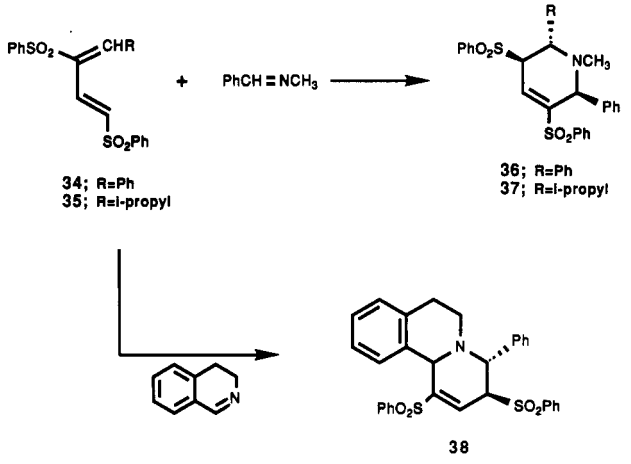
The formation of **31** can be attributed to an initial Diels–Alder cycloaddition followed by elimination of dimethylamine. Since 2*H*-thiopyran **31** represents an activated 1,3-cyclic diene, we decided to investigate its 4π-cycloaddition reactivity. Heating a sample of **31** in the

(38) MM2 calculations were performed on a VAX 8550 using Model 2.94 with the "statistical coordinate" option in TTY (i.e., CONF) to write the appropriate batch files for minimization with use of BAKMODEL to find the global minimum.

(39) *QCPE 506* (Ampac) using the AM1 Hamiltonian.

presence of benzylidenemethylamine afforded dihydropyridine **33** in 73% yield. Presumably, the reaction proceeds by an initial Diels–Alder cycloaddition to give **32**, which then undergoes a subsequent cycloreversion under the thermal conditions (150 °C) to produce thioformaldehyde and dihydropyridine **33**.

We also studied the 4 + 2 cycloaddition chemistry of several 4-substituted 1,3-bis(phenylsulfonyl)-1,3-butadienes. These compounds were prepared by treatment of a benzene solution of 1,3-bis(phenylsulfonyl)-1-propene (**23**) and an aldehyde in the presence of a catalytic amount of piperidine and acetic acid followed by azeotropic removal of water. This procedure was used to prepare dienes **34** and **35** starting from benzaldehyde and isobutyl aldehyde. Heating a sample of **34** or **35** with *N*-



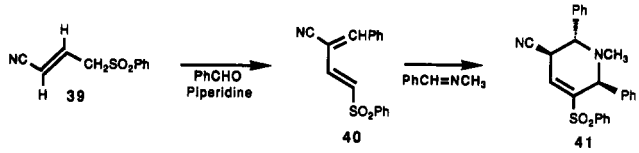
34; R=Ph
35; R=i-propyl

36; R=Ph
37; R=i-propyl

38

benzylidenemethylamine in methylene chloride at 50 °C for 24 h afforded cycloadducts **36** and **37** in 82% and 80% yield, respectively. A related reaction occurred with 3,4-dihydroisoquinoline and produced cycloadduct **38** in 93% yield. Once again, a 1,3-hydrogen shift from the initially formed cycloadduct nicely explains formation of the final product. It should be noted that the incorporation of a substituent onto the 4-position of the diene significantly diminished the rate of cycloaddition relative to the unsubstituted case.

The Diels–Alder behavior of 1-(phenylsulfonyl)-3-cyano-4-phenyl-1,3-butadiene (**40**) was also examined. Condensation of 1-cyano-3-(phenylsulfonyl)-1-propene (**39**) with benzaldehyde afforded diene **40** in 87% yield. Heating this compound with *N*-benzylidinemethylamine in toluene at 120 °C for 22 h gave tetrahydropyridine **41** in 93% isolated yield. In this case, the initially formed



cycloadduct does not undergo a 1,3-sigmatropic hydrogen shift. It is apparent from the elevated temperatures used to promote the reaction that a cyano group is much less effective in the facilitation of the 4 + 2 cycloaddition than a phenylsulfonyl group. This is presumably a consequence of the lower LUMO energy associated with the bis(phenylsulfonyl)-substituted diene.

The previous results are suggestive of a broad potential of the imine–bis(phenylsulfonyl)diene cycloaddition process. The bis(phenylsulfonyl)-functionalized dienes reported here should find use in organic synthesis of six-membered nitrogen heterocycles. Applications of these dienes in the arena of alkaloid synthesis are under current investigation in these laboratories and will be reported on at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV.

Preparation of 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1). A solution containing 17.1 g of *N*-chlorosuccinimide and 3.0 g of thiophenol in 100 mL of methylene chloride was heated at reflux under a nitrogen atmosphere. After heating for 5 min, 11.1 g of thiophenol was added dropwise at a rate so as to maintain a gentle reflux. The bright red-orange solution was stirred for an additional 30 min at 25 °C. The solution was filtered, and the mixture was added dropwise over 15 min to a cooled solution containing 5.0 g of 2-butyne-1,4-diol and 23.4 g of triethylamine in 150 mL of methylene chloride at −78 °C. The resulting solution was stirred at −78 °C for 1 h and was then allowed to warm to room temperature, after which 150 mL of water was added. The organic layer was separated and washed with water, a 1.0 N hydrochloric acid solution, a 10% sodium bicarbonate solution, and again with water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to leave behind a brown solid. This material was recrystallized from methanol to give 9.5 g (54% yield) of a white crystalline solid (mp 121–128 °C), which consisted of a mixture of the diastereomers of 2,3-bis(phenylsulfinyl)-1,3-butadiene: IR (KBr) 3080, 3055, 3005, 2960, 1580, 1475, 1445, 1365, 1035, 750, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz; isomer A) δ 5.60 (s, 2 H), 6.18 (s, 2 H), and 7.48 (m, 10 H); (isomer B) δ 5.85 (s, 2 H), 6.25 (s, 2 H), and 7.30 (m, 10 H).

To a stirred solution containing 10.0 g of the above solid in 300 mL of methylene chloride at 0 °C was added 14.3 g of *m*-chloroperoxybenzoic acid over a 5-min period. The solution was stirred at 0 °C for 2 h and was then allowed to slowly warm to room temperature. After being stirred for an additional 8 h at 25 °C, the solution was filtered and the filtrated was washed twice with a saturated aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The oily residue was recrystallized from methanol to give 8.8 g (79% yield) of a white crystalline solid, mp 183–184 °C, whose structure was assigned as 2,3-bis(phenylsulfonyl)-1,3-butadiene (1) on the basis of its spectral properties:[23] IR (KBR) 3120, 3060, 1585, 1445, 1310, 1150, 1070, 980, 755, 745, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 6.65 (s, 2 H), 6.80 (s, 2 H), and 7.2–7.7 (m, 10 H).

General Procedure for the Cycloaddition Reaction of Aldimines with 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1). A solution containing 0.50 g of 2,3-bis(phenylsulfonyl)-1,3-butadiene (1) and 1.5 mmol of the appropriate aldimine in 25 mL of methylene chloride was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure, and the crude solid that formed was recrystallized from a 50% methylene chloride–ether mixture to give the crystalline cycloadduct. Structures were assigned on the basis of their spectral properties.

3,5-Bis(phenylsulfonyl)-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (3): 81%, mp 172–173 °C; IR (KBr) 3105, 3000, 2890, 2810, 1590, 1475, 1450, 1325, 1310, 1210, 1150, 1090, 1060, 950, 770, 730, 700, and 625 cm^{-1}; NMR ($CDCl_3$, 260 MHz) δ 2.18 (s, 3 H), 2.86 (dd, 1 H, J = 13.3 and 6.1 Hz), 3.00 (dd, 1 H, J = 13.3 and 8.1 Hz), 4.29 (m, 1 H), 4.48 (s, 1 H), 6.32 (d, 2 H, J = 7.5 Hz), 6.83 (t, 2 H, J = 7.5 Hz), 7.05 (t, 1 H, J = 7.5 Hz), 7.42 (t, 1 H, J = 7.5 Hz), 7.48 (d, 1 H, J = 3.4 Hz), 7.61 (t, 2 H, J = 7.5 Hz), 7.78 (t, 1 H, J = 7.5 Hz), and 7.95 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 41.8, 44.8, 60.7, 63.3, 127.7, 127.8, 128.5, 129.4, 129.5, 130.1, 132.9, 134.2, 134.4, 137.0, 139.3, and 147.5. Anal. Calcd for $C_{24}H_{23}NO_4S_2$: C, 63.55; H, 5.11; N, 3.09. Found: C, 63.52; H, 5.16; N, 3.06.

1-Benzyl-3,5-bis(phenylsulfonyl)-2-phenyl-1,2,5,6-tetrahydropyridine (4): 90%, mp 185–186 °C; IR (KBr) 3070, 3040, 2880, 1450, 1320, 1305, 1150, 1085, 1025, 765, 750, 725, 705 and 690 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 3.00 (d, 2 H, J = 7.7 Hz), 3.32 (d, 1 H, J = 13.1 Hz), 3.56 (d, 1 H, J = 13.1 Hz), 4.27 (m, 1 H), 4.58 (s, 1 H), 6.32 (d, 2 H, J = 7.5 Hz), 6.85 (t, 2 H, J = 7.5 Hz), 7.05 (t, 1 H, J = 7.5 Hz), 7.14 (m, 2 H), 7.25–7.33 (m, 5 H), 7.41 (d, 2 H, J = 7.5 Hz), 7.47 (t, 1 H, J = 7.5 Hz), 7.54 (d, 1 H,

J = 2.9 Hz), 7.60 (t, 2 H, J = 7.5 Hz), 7.78 (t, 1 H, J = 7.5 Hz), and 7.87 (d, 2 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 42.2, 57.5, 59.8, 60.0, 127.6, 127.7, 127.9, 128.0, 128.5, 128.7, 128.9, 129.3, 129.4, 129.5, 130.5, 133.1, 134.3, 135.9, 136.6, 137.0, 139.1, and 147.3. Anal. Calcd for $C_{30}H_{27}NO_4S_2$: C, 68.03; H, 5.14; N, 2.64. Found: C, 68.27; H, 5.21; N, 2.87.

Reaction of 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1) with *N*-(1-Deuteriobenzylidene)benzylamine. A solution containing 399 mg of diene 1 and 238 mg of *N*-(1-deuteriobenzylidene)-benzylamine in 10 mL of methylene chloride was stirred at 25 °C for 20 h. The solvent was removed under reduced pressure to leave behind a clear oil that crystallized on standing. Recrystallization of the solid from methylene chloride–hexane gave 510 mg (81%) of 2-deuterio-3,5-bis(phenylsulfonyl)-1-benzyl-2-phenyl-1,2,5,6-tetrahydropyridine (**5**) as a white crystalline solid: mp 181–182 °C: IR (KBr) 3070, 3040, 2880, 1450, 1320, 1305, 1085, 1025, 765, 750, 725, 705, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.00 (d, 2 H, J = 7.7 Hz), 3.32 (d, 1 H, J = 13.1 Hz) 3.56 (d, 1 H, J = 13.1 Hz), 4.18–4.32 (m, 1 H), 6.32 (d, 2 H, J = 7.3 Hz), 6.85 (t, 2 H, J = 7.7 Hz), 7.05 (t, 1 H, J = 7.5 Hz), 7.14–7.60 (m, 13 H), 7.78 (t, 1 H, J = 7.5 Hz), and 7.85 (d, 2 H, J = 7.3 Hz); MS m/e ($M+H^+$) 531.

1-Benzyl-3,5-bis(phenylsulfonyl)-2-α-naphthyl-1,2,5,6-tetrahydropyridine (6): 75%; mp 210–211 °C; IR (KBr) 3060, 2900, 2840, 1450, 1320, 1310, 1160, 1150, 1090, 755, 695, and 620 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.07 (d, 2 H, J = 7.6 Hz), 3.62 (d, 1 H, J = 12.7 Hz), 3.70 (d, 1 H, J = 12.7 Hz), 4.33 (t, 1 H, J = 7.6 Hz), 5.40 (s, 1 H), 5.71 (d, 1 H, J = 7.5 Hz), 6.48 (t, 1 H, J = 7.5 Hz), 7.03 (d, 1 H, J = 8.6 Hz), 7.13–7.24 (m, 5 H), 7.30–7.50 (m, 8 H), 7.62 (t, 2 H, J = 7.5 Hz), 7.71 (d, 2 H, J = 8.6 Hz), 7.79 (t, 1 H, J = 7.5 Hz), and 7.89 (d, 2 H, J = 7.5 Hz). Anal. Calcd for $C_{34}H_{29}NO_4S_2$: C, 70.44; H, 5.04; N, 2.42. Found: C, 70.38; H, 5.08; N, 2.41.

Preparation of 2,3-Bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (7). A solution containing 2.01 g of (*o*-nitrophenyl)-sulfenyl chloride in 30 mL of methylene chloride was added to a cooled solution containing 0.53 g of butyne-1,4-diol and 2.48 g of triethylamine in 40 mL methylene chloride at −78 °C. After being stirred for 1 h at −78 °C, the reaction mixture was allowed to warm to 25 °C and then 100 mL of water was added to the solution. The aqueous layer was separated and extracted with methylene chloride. The organic layer was washed with water, a 1.0 N hydrochloric acid solution, a saturated sodium bicarbonate solution, and water and then dried over sodium sulfate. Concentration of the solution under reduced pressure left a yellow solid that was recrystallized from methanol to give 1.80 g (75%) of 2,3-bis[(*o*-nitrophenyl)sulfinyl]-1,3-butadiene (**12**) as a 2:1 mixture of diastereomers: IR (KBr) 3095, 1590, 1565, 1515, 1505, 1490, 1335, 1310, 1065, 1035, 920, 730, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz, minor) δ 5.51 (s, 2 H), 6.13 (s, 2 H), and 7.35–8.38 (m, 8 H); (major) δ 6.13 (s, 2 H), 6.30 (s, 2 H), and 7.35–8.38 (m, 8 H). This mixture was used in the next step without any further purification.

A 4.37 g sample of *m*-chloroperbenzoic acid was slowly added over 10 min to a solution containing 3.45 g of 2,3-bis[(*o*-nitrophenyl)sulfinyl]-1,3-butadiene (**12**) in 60 mL of chloroform. The mixture was heated at reflux for 16 h, allowed to cool to room temperature, and was then washed with a saturated sodium bicarbonate solution followed by water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to leave behind a yellow solid. This material was recrystallized from methanol–chloroform to give 2.93 g of a yellow solid whose structure was assigned as 2,3-bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (**7**): mp 193–194 °C; IR (KBr) 3135, 1535, 1345, 1315, 1305, 1170, 1140, 1115, 1080, 855, 750, 735, and 705 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 6.60 (s, 2 H), 6.85 (s, 2 H), 7.65–7.78 (m, 6 H), and 8.07–8.14 (m, 2 H). Anal. Calcd for $C_{16}N_{12}N_2O_8S_2$: C, 45.28; H, 2.85; N. 6.60. Found: C, 45.34; H, 2.89; N, 6.57.

Reaction of 2,3-Bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (7) with *N*-Benzylidenemethylamine. A solution containing 347 mg of butadiene **7** and 0.1 mL of *N*-benzylidenemethylamine in 6 mL of methylene chloride was stirred for 24 h at 25 °C. The solvent was removed under reduced pressure to leave behind a yellow oil that crystallized on standing. Recrystallization of the solid from methylene chloride–methanol gave 325 mg (73%) of 3,5-bis[(o-nitrophenyl)sulfonyl]-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (**13**) as a yellow crystalline compound: mp 169–170 °C; IR (KBr) 3105, 2950, 1545, 1375, 1330, 1145, 1025, 780, 745, 730, 670, and 620 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3 H), 3.04 (dd, 1 H, J = 13.3 and 5.5 Hz), 3.59 (dd, 1 H, J = 13.3 and 5.5 Hz), 4.57 (s, 1 H), 5.03–5.16 (m, 1 H), 6.95–7.10 (m, 3 H), 7.15–7.38 (m, 5 H), 7.50 (t, 1 H, J = 7.4 Hz), 7.65 (d, 1 H, 8.1 Hz), 7.85–8.00 (m, 3 H), and 8.59 (d, 1 H, J = 7.3 Hz). Anal. Calcd for $C_{24}H_{21}N_3O_8S_2$: C, 53.03; H, 3.89; N, 7.73. Found: C, 52.97; H, 3.92; N, 7.68.

Reaction of 2,3-Bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (7) with *N*-Benzylidenebenzylamine. A solution containing 228 mg of diene **7** and 0.1 mL of *N*-benzylidenebenzylamine in 5 mL of methylene chloride was stirred for 44 h at 25 °C. Removal of the solvent under reduced pressure followed by silica gel chromatography of the crude residue using a 1:1 mixture of ethyl acetate–hexane as the eluent gave 206 mg (62%) of 1-benzyl-3,5-bis[(*o*-nitrophenyl)sulfonyl]-2-phenyl-1,2,5,6-tetrahydropyridine (**14**) as a yellow crystalline solid; mp 175–176 °C; IR (KBr) 3100, 3040, 2920, 1600, 1550, 1462, 1370, 1345, 1160, 1130, 1030, 930, 750, and 710 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.13 (dd, 1 H, J = 13.7 and 5.8 Hz), 3.63 (dd, 1 H, J = 13.7 and 5.8 Hz), 3.64 (d, 2 H, J = 9.1 Hz), 4.75 (s, 1 H), 5.12–5.18 (m, 1 H), 6.98–7.10 (m, 3 H), 7.15–7.40 (m, 10 H), 7.45 (t, 1 H, J = 7.4 Hz), 7.62 (d, 1 H, J = 8.1 Hz), 7.85–7.95 (m, 3 H), and 8.47–8.55 (m, 1 H). Anal. Calcd for $C_{30}H_{25}N_3O_8S_2$: C, 58.15, H. 4.07; N, 6.78. Found: C, 58.22; H, 4.12; N, 6.75.

Reaction of 2,3-Bis(phenylsulfonyl)-1,3-butadiene (1) and 2,3-Bis[(*o*-nitrophenyl)sulfonyl]-1,3-butadiene (7) with *N*-Benzylidenemethylamine. A solution containing 224 mg of diene 1, 254 mg of diene **7**, and 0.16 mL of *N*-benzylidene-methylamine in 10 mL of methylene chloride was stirred at 25 °C for 24 h. The solvent was removed under reduced pressure to leave behind an orange oil that was chromatogaphed on a silica gel plate with a 2:3 mixture of ethyl acetate–hexane as the eluent. One of the major fractions isolated contained 150 mg of a yellow solid whose structure was assigned as 3,5-bis(phenylsulfonyl)-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (**3**), mp 172–173 °C. Another fraction contained 98 mg of 3,5-bis[(*o*-nitrophenyl)-sulfonyl]-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (**13**), mp 169–170 °C. The third fraction was a viscous oil whose structure was assigned as 1-methyl-5-[(*o*-nitrophenyl)sulfonyl]-2-phenyl-3-(phenylsulfonyl)-1,2,5,6-tetrahydropyridine (**19**): IR (KBr) 3100, 3070, 1545, 1450, 1370, 1325, 1310, 1150, 1125, 1085, 915, 855, 730, 705, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.18 (s, 3 H), 2.84 (dd, 1 H, J = 13.3 and 5.6 Hz), 3.26 (dd, 1 H, J = 13.3 and 7.0 Hz), 4.49 (s, 1 H), 4.95–5.05 (m, 1 H), 6.85–7.65 (m, 11 H), 7.75–8.00 (m, 3 H), and 8.13 (d, 1 H, J = 8.4 Hz); MS m/e ($M + H^+$) 499. Anal. Calcd for $C_{24}H_{22}N_2O_6S_2$: C, 57.82, H. 4.45; N, 5.62. Found: C, 57.56; H, 4.32; N, 5.75.

Preparation of 1,3-Bis(phenylsulfonyl)-1,3-butadiene (17). A mixture containing 21.7 g of 3-bromo-1-(phenylsulfonyl)-1-propene[35] and 25 g of the sodium salt of benzenesulfinic acid in 200 mL of methanol was heated at reflux for 35 min. The mixture was cooled, and 100 mL of a saturated aqueous ammonium chloride solution was added. The organic layer was extracted with methylene chloride and then washed with a saturated aqueous sodium bicarbonate solution followed by water. The solution was dried over sodium sulfate and concentrated under reduced pressure to leave behind a white solid that was recrystallized from methylene chloride to give 22.0 g (82%) of 1,3-bis(phenylsulfonyl)-1-propene (**23**): mp 106–107 °C (lit.[35] mp 102–103 °C); IR (KBr) 3060, 2830, 1445, 1310, 1280, 1150, 1085, 850, 740, 720, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.93 (d, 2 H, J = 7.8 Hz), 6.34 (d, 1 H, J = 15 Hz), 6.77 (dt, 1 H, J = 15 and 7.8 Hz), and 7.35–8.00 (m, 10 H).

To a solution containing 2.81 g of disulfone **23** in 85 mL of dimethoxyethane at −78 °C was added 5.5 mL of a 1.6 M *n*-butyllithium solution. After the solution was stirred for 20 min at −78 °C, 266 mg of formaldehyde was bubbled through the reaction mixture by use of a stream of nitrogen. Stirring was continued for 1 h at −78 °C, and then the reaction mixture was added to 50 mL of a saturated ammonium chloride solution. The aqueous layer was separated and extracted with methylene chloride. The organic layer was washed with a saturated sodium bicarbonate solution and water and then dried over sodium sulfate. Removal of the solvent under reduced pressure followed by silica gel

chromatography of the crude residue using a 2:3 mixutre of ethyl acetate–hexane as the eluent gave 2.34 g (76%) of 1,3-bis(phenylsulfonyl)-1-buten-4-ol (**24**) as a yellow oil that was used in the next step without further purification: IR (neat) 3520, 3075, 2940, 1590, 1450, 1310, 1150, 1085, 1025, 735, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.53 (t, 1 H, J = 6.5 Hz, D_2O exchangeable), 4.09–4.20 (m, 3 H), 6.85 (t, 1 H, J = 8.3 Hz), and 7.40–8.00 (m, 11 H); MS m/e (M + Li^+) 359.

The other minor component present (600 mg, 20%) was a yellow oil whose structure was assigned as of 2,4-bis(phenylsulfonyl)-2-pentene-1,5-diol (**25**): IR (neat) 3505, 3080, 2940, 2900, 1645, 1590, 1450, 1310, 1150, 1085, 725, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.80 (b s, 1 H, D_2O exchangeable), 3.05 (b s, 1 H, D_2O exchangeable), 3.90–4.30 (m, 4 H), 4.42 (dt, 1 H, J = 10.6 and 5.5 Hz), 6.85 (d, 1 H, J = 10.7 Hz), and 7.25–8.00 (m, 10 H); MS m/e (M + Li^+) 389. A higher yield of this diol could be obtained (60%) by use of 10 equiv of formaldehyde. When a sample of the diol was subjected to silica gel chromatography, it rearranged to give 3,5-bis(phenylsulfonyl)-5,6-dihydro-2*H*-pyran (**26**) as a pale yellow oil: IR (neat) 3070, 2920, 2870, 1645, 1585, 1480, 1450, 1315, 1215, 1155, 1085, 1020, 1005, 955, 870, and 750 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 37.5–3.98 (m, 3 H), 4.02–4.29 (m, 2 H), 7.05–7.15 (m, 1 H), 7.41 (t, 2 H, J = 7.7 Hz), 7.50–7.85 (m, 8H); HRMS cacld for $C_{17}H_{16}O_5S_2$ 364.0439, found 364.0440. Anal. Calcd for $C_{17}H_{16}O_5S_2$: C, 56.04; H, 4.43. Found: C, 55.87; H, 4.52.

A solution containing 244 mg of 1,3-bis(phenylsulfonyl)-1-buten-4-ol (**24**) and 0.15 mL of phosphorus tribromide was heated at 80 °C for 20 min and was then allowed to cool to room temperature. The mixture was taken up in ether, and a slight excess of triethylamine was added. To the resulting suspension was added 10 mL of ice water, and the mixture was extracted with ether. The combined ether extracts were washed with a saturated sodium bicarbonate solution and water and then dried over sodium sulfate. Concentration of the solution under reduced pressure left 163 mg (71%) of 1,3-bis(phenylsulfonyl)-1,3-butadiene (**17**) as a clear but very reactive oil: IR ($CHCl_3$) 3060, 2940, 2850, 1445, 1325, 1150, 1085, 1020, 975, 910, 845, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 6.26 (s, 1 H), 6.71 (s, 1 H), 7.00 (d, 1 H, J = 15.6 Hz), 7.23 (d, 1 H, J = 15.6 Hz), 7.35–7.75 (m, 6 H), 7.75–7.95 (m, 4 H). The diene was too labile to leave around for any significant period of time and was treated with the appropriate imine to produce the Diels–Alder cycloadduct, as outlined in the following text.

Diels–Alder Reaction of 1,3-Bis(phenylsulfonyl)-1,3-butadiene (17) with Various Imines. A solution containing 69 mg of 1,3-bis(phenylsulfonyl)-1,3-butadiene (**17**) and 0.03 mL of *N*-benzylidenemethylamine in 8 mL of methylene chloride was stirred at 25 °C for 2 h. Concentration of the reaction mixture followed by recrystallization of the crude solid from methylene chloride–ether afforded 82 mg (88%) of 3,5-bis(phenylsulfonyl)-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (**3**) as a yellow solid, mp 172–173 °C, which was identical with a sample of **3** obtained from the reaction of 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**) with the same imine. The reaction between 1,3-butadiene **17** and a number of other arylimines afforded the same cycloadducts as described for the reaction with 2,3-bis(phenylsulfonyl)-1,3-butadiene (**1**).

To a solution containing 193 mg of 1,3-bis(phenylsulfonyl)-1,3-butadiene (**17**) in 5 mL of methylene chloride was added 1 equiv of *N*-propylidenebenzylamine[40] in 1 mL of methylene chloride. The solution was stirred at 25 °C under nitrogen for 12 h. Removal of the solvent under reduced pressure left behind a yellow oil. Purification of this material by silica gel chromatography with a 1:2 ethyl acetate–hexane mixture as the eluent afforded 132 mg (68%) of 1-benzyl-3,5-bis(phenylsulfonyl)-2-ethyl-1,2,5,6-tetrahydropyridine (**30**) as a white solid: mp 159–160 °C; IR (KBr) 3060, 2970, 2940, 1640, 1620, 1585, 1500, 1450, 1385, 1320, 1310, 1150, 1085, 1025, 1000, 980, 750, 740, 725, and 690 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.55–0.80 (m, 4 H), 1.35–1.52 (m, 1 H), 2.88 (b d, 1 H, J = 9.7 Hz), 3.02 (d, 1 H, J = 13.1 Hz), 3.10–3.25 (m, 2 H), 3.41 (d, 1 H, J = 13.1 Hz), and 7.74–7.92 (m, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 10.40, 25.32, 41.0, 56.23, 56.63, 56.73, 126.83, 127.51, 127.61, 127.98, 128.64, 128.73, 128.87, 133.19, 133.94, 135.10, 136.56, 138.21, and 148.79. Anal. Calcd for $C_{28}H_{28}NO_4S_2$: C, 64.84; H, 5.65; N, 2.91. Found: C, 64.73; H, 5.70; N, 2.91.

Reaction of 1,3-Bis(phenylsulfonyl)-1,3-butadiene (17) with *N,N*-Dimethylthioformamide. To a solution containing 85 mg of 1,2,4-tris(phenylsulfonyl)-2-butene (**28**)[34] and 0.02 mL of *N,N*-dimethylthioformamide in 7 mL of benzene was added 1 equiv of triethylamine in 1 mL of benzene. The solution was heated at reflux under nitrogen for 20 h. The reaction mixture was filtered through a pad of silica gel followed by removal of the solvent under reduced pressure to leave behind an orange residue. Purification of the oil by silica gel chromatography with an ethyl acetate–hexane (30:70) mixture as the eluent afforded 53 mg (78%) of 3,5-bis(phenylsulfonyl)-2*H*-thiopyran (**31**): mp 187–188 °C; IR (KBr) 3060, 1620, 1585, 1530, 1450, 1320, 1155, 1090, 790, 755, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.50 (s, 2 H), 7.32 (s, 1 H), 7.50–7.70 (m, 6 H), and 7.78–7.98 (m, 5 H). Anal. Calcd for $C_{16}H_{14}O_4S_3$: C, 53.93; H, 3.73. Found: C, 53.81; H, 3.76.

A solution containing 101 mg of 2*H*-thiopyran **31** and 0.04 mL of *N*-benzylidenemethylamine in 6 mL of toluene was heated at 150 °C in a sealed tube for 52 h. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 76 mg (73%) of 3,5-bis(phenylsulfonyl)-1-methyl-2-phenyl-5,6-dihydropyridine (**33**) as a yellow solid: mp 192–193 °C; IR (KBr) 3040, 2920, 1625, 1545, 1480, 1445, 1385, 1305, 1210, 1140, 1085, 1030, 885, 830, 760, 720, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.98 (s, 3 H), 5.43 (s, 1 H) 7.00–7.10 (m, 4 H), 7.10–7.25 (m, 3 H), 7.27–7.37 (m, 1 H), 7.37–7.50 (m, 3 H), 7.58–7.68 (m, 4 H), and 7.89–7.98 (m, 2 H); MS m/e (M + H) 452. Anal. Calcd for $C_{24}H_{21}NO_4S_2$: C, 63.83; H, 4.69; N, 3.10. Found: C, 63.59; H, 4.78; H, 3.04.

Preparation and Cycloaddition Behavior of 1,3-Bis(phenylsulfonyl)-4-phenyl-1,3-butadiene (34). A mixture containing 0.1 mL of piperidine, 0.1 mL of glacial acetic, 4.04 g of 1,3-bis(phenylsulfonyl)-1-propene (**23**), and 1.44 g of benzaldehyde in 30 mL of benzene was heated at reflux for 4 h with a Dean-Stark apparatus. At the end of this time, the mixture was added to 40 mL of a saturated ammonium chloride solution. The aqueous layer was extracted with methylene chloride, and the organic extracts were washed with a saturated sodium bicarbonate solution and water and then dried over sodium sulfate. Concentration of the solution left a pale yellow solid that was recrystallized from methylene chloride–hexane to give 4.15 g (81%) of 1,3-bis(phenylsulfonyl)-4-phenyl-1,3-butadiene (**34**): mp 149–150 °C; IR (KBr) 3080, 3050, 1640, 1450, 1325, 1310, 1290, 1155, 1145, 1085, 860, 855, 785, and 695 cm^{-1}; NMR ($CDCl_3$, 300 Mhz) δ 7.20–7.58 (m, 12 H), 7.62–7.78 (m, 5 H), and 8.19 (s, 1 H). Anal. Calcd for $C_{22}H_{18}O_4S_2$: C, 64.38; H, 4.42. Found: C, 64.21; H, 4.29.

A solution containing 271 mg of the above diene **34** and 0.08 mL of *N*-benzylidenemethylamine in 10 mL of methylene chloride was heated at 50 °C for 24 h. Removal of the solvent under reduced pressure left a white solid that was recrystallized from methylene chloride–hexane to give 285 mg (82%) of 3,5-bis(phenylsulfonyl)-2,6-diphenyl-1-methyl-1,2,5,6-tetrahydropyridine (**36**) as a white crystalline solid: mp 174–175 °C; IR (KBr) 3075, 2960, 1595, 1500, 1450, 1320, 1310, 1210, 1155, 1140, 1085, 880, 760, 735, 710, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.76 (s, 3 H), 4.36 (s, 1 H) 4.41–4.51 (m, 2 H), 6.45 (d, 2 H, J = 7.3 Hz), 6.80 (t, 2 H, J = 7.6 Hz), 6.99 (t, 1 H, J = 7.3 Hz), 7.05–7.70 (m, 14 H), and 7.83 (d, 2 H, J = 7.6 Hz); HRMS calcd for $C_{30}H_{27}NO_4S_2$ 529.1382, found 529.1376. Anal. Calcd for $C_{30}H_{27}NO_4S_2$: C, 68.04; H, 5.14; N, 2.65. Found: C, 67.87; H, 5.02; N, 2.51.

In a related example, a solution containing 207 mg of diene **34** and 89 mg of 3,4-dihydroisoquinoline[41] in 10 mL of methylene chloride was heated at 50 °C for 24 h. Removal of the methylene chloride under reduced pressure left an orange oil that crystallized upon standing. Recrystallization of the solid from methylene chloride–ether gave 255 mg (93%) of 1,3-bis(phenylsulfonyl)-4-phenyl-3,4,6,7-tetrahydro-11b*H*-benzo[*a*]quinoline (**38**) as a white solid: mp 176–177 °C; IR (KBr) 3070, 2940, 1640, 1590, 1500, 1450, 1320, 1310, 1150, 1135, 1085, 760, and 745 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.64–3.00 (m, 4 H), 4.51–4.58 (m, 2 H), 4.83 (d, 1 H, J = 4.4 Hz), 6.64 (d, 2 H, J = 7.4 Hz), 6.78 (t, 2 H, J = 7.4 Hz),

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7.10–7.19 (m, 10 H), 7.39–7.47 (m, 1 H), 7.56 (t, 2 H, J = 7.6 Hz), 7.71 (t, 1 H, J = 7.4 Hz), and 7.92 (d, 2 H, J = 7.6 Hz). Anal. Calcd for $C_{31}H_{27}NO_4S_2$: C, 68.74; H, 5.02; N, 2.59. Found: C, 68.81; H, 5.09; N, 2.57.

Preparation and Cycloaddition Behavior of 1,3-Bis(phenylsulfonyl)-4-isopropyl-1,3-butadiene (35). A mixture containing 0.05 mL of piperidine, 0.05 mL of glacial acetic, 2.48 g of 1,3-bis(phenylsulfonyl)-1-propene (**23**) and 0.70 mL of isobutyraldehyde in 80 mL of a 4:1 benzene–pentane mixture was heated at reflux for 40 h by use of a Dean-Stark apparatus. At the end of this time, the mixture was allowed to cool and was added to 40 mL of a saturated ammonium chloride solution. The aqueous layer was extracted with methylene chloride, and the organic extracts were washed with a saturated sodium bicarbonate solution and water and then dried over sodium sulfate. The solution was concentrated under reduced pressure, 20 mL of ether was added, and the mixture was allowed to crystallize. The resulting solid was recrystallized from methylene chloride–ether to give 2.31 g (80%) of 1,3-bis(phenylsulfonyl)-4-isopropyl-1,3-butadiene (**35**): mp 121–122 °C; IR (KBr) 3070, 2975, 1635, 1585, 1450, 1385, 1310, 1285, 1215, 1250, 1085, 975, 860, 845, 760, 725, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.12 (d, 6 H, J = 6.5 Hz), 2.80–2.90 (m, 1 H), 7.19 (d, 1 H, J = 10.5 Hz), and 7.30–7.95 (m, 12 H). Anal. Calcd For $C_{19}H_{20}O_4S_2$: C, 60.63; H, 5.36. Found: C, 60.47; H, 5.02.

A solution containing 104 mg of diene **35** and 0.04 mL of N-benzylidenemethylamine in 7 mL of methylene chloride was heated at 25 °C for 24 h. Removal of the solvent under reduced pressure followed by silica gel chromatography of the crude residue using a 2:3 ethyl acetate–hexane mixture as the eluent gave 110 mg (80%) of 3,5-bis(phenylsulfonyl)-6-isopropyl-1-methyl-2-phenyl-1,2,5,6-tetrahydropyridine (**37**) as a white crystalline solid: mp 161–162 °C; IR (KBr) 3070, 3040, 2960, 1445, 1315, 1305, 1220, 1155, 1145, 1085, 1055, 860, 690, and 660 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.89 (d, 3 H, J = 6.8 Hz), 0.97 (d, 3 H, J = 6.8 Hz), 1.97 (s, 3 H), 2.20–2.32 (m, 1 H), 3.46 (d, 1 H, J = 4.9 Hz), 4.00–4.10 (m, 1 H), 4.55 (s, 1 H), 6.30 (b s, 2 H), 6.69 (t, 2 H, J = 7.4 Hz), 6.91 (t, 1 H, J = 7.4 Hz), 7.05–7.15 (m, 3 H), 7.25–7.40 (m, 2 H), 7.42–7.70 (m, 4 H), and 7.85 (d, 2 H, J = 7.7 Hz). Anal. Calcd for $C_{27}H_{29}NO_4S_2$: C, 65.43; H, 5.90; N, 2.83. Found: C, 65.31; H, 5.92; N, 2.77.

Preparation and Cycloaddition Behavior of 1-(Phenylsulfonyl)-3-cyano-4-phenyl-1,3-butadiene (40). To a solution containing 500 mg of 4-(phenylsulfonyl)-2-butenenitrile (**39**) and 256 mg of freshly distilled benzaldehyde in 10 mL of dry benzene was added one drop of piperidine and one drop of glacial acetic acid. The reaction was heated at reflux in a Dean-Stark apparatus for 14 h. At the end of this time, the solution was taken up in ether and the organic phase was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a yellow solid. Recrystallization from 70% chloroform–hexane gave 620 mg (87%) yield) of pale yellow solid, mp 163–164 °C, whose structure was assigned as 1-(phenylsulfonyl)-3-cyano-4-phenyl-1,3-butadiene (**40**) on the basis of its spectral properties: IR ($CHCl_3$) 3060, 2365, 1610, 1595, 1450, 1320, 1155, 1090, 1025, 970, 845, 810, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 6.85 (d, 1 H, J = 14.9 Hz), 7.38–7.67 (m, 8 H), and 7.85–7.96 (m, 4 H); HRMS calcd for $C_{17}H_{13}NO_2S$ 295.0667, found 295.0657. Anal. Calcd for $C_{17}H_{13}NO_2S$: C, 69.14; H, 4.44; N, 4.75. Found: C, 69.36; H, 4.51; N, 4.77.

A solution containing 250 mg of diene **40** and 100 mg of N-benzylidenemethylamine in 20 mL of toluene was heated at 120 °C in a sealed tube for 22 h. The solvent was removed under reduced pressure, and the crude solid that formed was recrystallized from 50% methylene chloride–ether to give 330 mg (94% yield) of a yellow solid, mp 172–173 °C, whose structure was assigned as 1-methyl-3-cyano-2,6-diphenyl-5-(phenylsulfonyl)-1,2,5,6-tetrahydropyridine (**41**) on the basis of its spectral properties: IR ($CHCl_3$) 3010, 2990, 2235, 1605, 1450, 1310, 1145, 1085, 1020, 910, 880, and 845 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.85 (s, 3 H), 3.66 (m, 1 H), 4.21 (m, 1 H), 4.78 (m, 1 H), 6.52 (d, 2 H, J = 7.4 Hz), 6.99 (dd, 1 H, J = 5.1 and 1.9 Hz), and 7.10–7.95 (m, 13 H). Anal. Calcd for $C_{25}H_{22}N_2O_2S$: C, 72.44; H, 5.35; N, 6.76. Found: C, 72.27; H, 5.31; N, 6.73.

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Supplementary Material Available: The final positional and thermal parameters of cycloadduct **3** (5 pages). Ordering information is given on any current masthead page.

Synthesis and Properties of New π-Donor Sulfur Heterocycles

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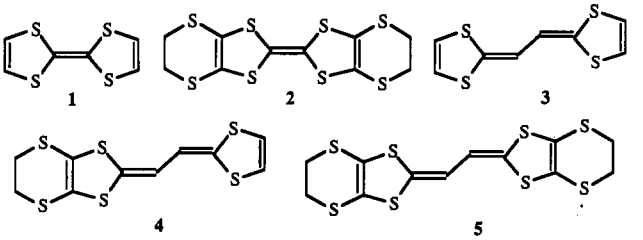
Two new π-donors related to bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **2**) have been synthesized. These are the vinylogue **5** of BEDT-TTF and the mixed-vinylogue **4** related to TTF and BEDT-TTF.

High, one-dimensional electrical conductivity was reported for a tetracyanoquinodimethane (TCNQ) complex with tetrathiafulvalene (TTF, **1**) in 1973.[1] This observation spurred a tremendous synthetic effort with the aim of discovering new and better π-donors. Subsequent work had led to scores of TTF analogues. The most investigated of these to date is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, **2**), certain cation radical salts of which show superconducting behavior.[2-4]

One of the more interesting of the TTF-related structures is the TTF vinylogue, ethanediylidene-2,2′-bis(1,3-dithiole) (**3**), reported in 1983.[5] We now describe the synthesis and some properties of the mono(ethylenedithio)



(**4**) and the bis(ethylenedithio) (**5**) derivatives of the TTF vinylogue **3**.

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