H, H5'), 3.76 (dd, J = 6.4, 8.6 Hz, 1 H, H6'), 3.66 (dd, J = 3.6, 8.5 Hz, 1 H, H4'), 3.39 (dd, J = 5.5, 9.8 Hz, 1 H, CH_2I), 3.21 (dd, J = 7.7, 9.8 Hz, 1 H, CH_2I), 2.98 (dd, J = 8.6, 4.9 Hz, 1 H, H6'), 2.93 (m, 1 H, H4), 2.17 (ddd, J = 7.3, 8.6, 12.7 Hz, 1 H, H4), 1.42 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 1.27 (s, 6 H, $2CH_3$); ^{13}C NMR δ 140.5, 128.8, 127.7, 127.0, 112.5 (C), 109.2 (C), 99.8 (C1'), 83.8 (CH), 82.4 (CH), 80.2 (CH), 77.8 (CH), 72.6 (CH), 68.6 (C3), 66.5 (C6'), 46.1 (C4), 26.5 (CH_3), 25.8 (CH_3), 25.1 (CH_3), 24.4 (CH_3), 6.53 (CH_2I); MS m/z (relative intensity) 531 (72, M^+), 430 (18), 318 (32), 185 (50), 141 (34), 129 (62), 104 (38), 101 (75), 91 (45), 85 (46), 69 (31), 59 (44), 43 (100).

(3*S*,5*R*)-*N*-(2',3':5',6'-*O*-Diisopropylidene-α-D-mannofuranosyl)-3-phenyl-5-(iodomethyl)isoxazolidine (9): $[\alpha]^{22}_D$ +115.8° (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.35 (m, 5 H, ArH), 5.04 (dd, J = 0.5, 6.6 Hz, 1 H, H2'), 4.92 (dd, J = 4.0 Hz, 6.6 Hz, 1 H, H3'), 4.55 (d, J = 0.5 Hz, 1 H, H1'), 4.43 (dd, J = 7.2, 9.9 Hz, 1 H), 4.35 (m, 3 H,), 4.15 (m, 2 H,), 3.45 (dd, J = 6.7, 9.8 Hz, 1 H, CH_2I), 3.29 (dd, J = 6.9, 9.8 Hz, 1 H, CH_2I), 2.68 (dt, J = 7.0, 12.5 Hz, 1 H, H4), 2.10 (ddd, J = 6.6, 10.0, 12.5 Hz, 1 H, H4), 1.53 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3); ^{13}C NMR δ 137.8, 128.9, 128.3, 128.0, 112.5 (C), 109.2 (C), 94.4 (C1'), 85.0 (CH), 84.8 (CH), 80.5 (CH), 77.1 (CH), 73.9 (CH), 66.7 (C6'), 63.9 (C3), 45.2 (C4), 26.7 (CH_3), 25.7 (CH_3), 25.1 (CH_3), 24.0 (CH_3), 8.4 (CH_2I); high-resolution mass spectrum for $C_{22}H_{30}NO_6I$ calcd 531.11179, found 531.11093; MS m/z (relative intensity) 531 (61, M^+), 516 (26), 430 (51), 318 (52), 257 (30), 185 (87), 130 (47), 129 (65), 101 (70), 91 (29), 85 (48), 59 (43), 43 (100).

(3*S*,5*S*)-*N*-(2',3':5',6'-*O*-Diisopropylidene-α-D-mannofuranosyl)-3-phenyl-5-(iodomethyl)isoxazolidine (10): $[\alpha]^{22}_D$ +85.6° (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.32 (m, 5 H, ArH), 5.30 (s, 1 H, H1'), 5.01 (d, J = 6.0 Hz, 1 H, H2'), 4.90 (dd, J = 4.1, 6.0 Hz, 1 H, H3'), 4.51 (dd, J = 4.1, 7.9 Hz, 1 H), 4.48 (s, 1 H), 4.39 (t, J = 5.5 Hz, 1 H), 4.32 (m, 1 H), 4.16 (m, 3 H), 3.35 (dd, J = 5.5, 10.6 Hz, 1 H, CH_2I), 3.29 (dd, J = 4.8, 10.6 Hz, 1 H, CH_2I), 2.40 (m, 2 H, H4), 1.52 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3); ^{13}C NMR δ 137.8, 128.9, 128.3, 127.0, 112.4 (C), 109.3 (C), 93.5 (C1'), 85.1 (CH), 84.8 (CH), 80.5 (CH), 75.6 (CH), 73.8 (CH), 67.0 (CH_2), 62.5 (C3), 44.3 (C4), 26.7 (CH_3), 25.7 (CH_3), 25.3 (CH_3), 24.0 (CH_3), 7.9 (CH_2I); MS m/z (relative intensity) 531 (74, M^+), 516 (26), 430 (38), 318 (47), 257 (21), 185 (56), 129 (41), 101 (50), 91 (26), 85 (38), 59 (32), 43 (100); high-resolution mass spectrum for $C_{22}H_{30}NO_6I$ calcd 531.11179, found 531.11146.

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(Nitroaryl)sulfinyl-Substituted Allenes. Novel and Convenient Propargyl Alcohol Synthons in 4 + 2 Cycloaddition Chemistry

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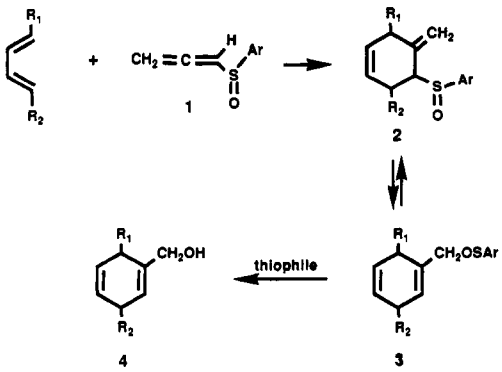
(Nitroaryl)sulfinyl-substituted allenes are conveniently prepared by treating propargyl alcohol or methyl 3-hydroxy-2-butynoate with a (nitroaryl)sulfenyl chloride and triethylamine. These activated allenes undergo 4 + 2 cycloaddition across the C_1C_2 π-bond. The initially formed allylic sulfoxide readily undergoes a 2,3-sigmatropic rearrangement to produce a stable sulfenate ester that is easily cleaved with thiophilic reagents. The dienophilic reactivity of the (nitroaryl)sulfinyl-substituted allene is much greater than the corresponding propargyl alcohol, and the cycloaddition also proceeds with high regioselectivity. The Diels-Alder reaction of [(2-nitrophenyl)sulfinyl]propadiene with Danishefsky's diene affords meta-substituted benzyl alcohols in high yield. Reaction of the more highly activated methyl 2-[(2-nitrophenyl)sulfinyl]-2,3-butadienoate with Danishefsky's diene followed by treatment of the resulting sulfenate ester with triethyl phosphite produces substituted phthalides in excellent yield. The (2,4-dinitrophenyl)sulfinyl-substituted allene was found to react smoothly with a variety of nitrones to give sulfenate esters of isoxazolidines. These allenyl sulfoxides correspond to formal equivalents of propargyl alcohol, which itself is too unreactive to undergo Diels-Alder chemistry or 1,3-dipolar cycloaddition with nitrones or nitrile oxides.

4 + 2 cycloadditions represent one of the most efficient methods for generating complex ring systems.[1-5] Two useful examples of this class are the Diels-Alder and 1,3-dipolar cycloaddition reactions. A limitation of these reactions is the poor reactivity of unactivated acetylenes with most 1,3-dienes and 1,3-dipoles, preventing the introduction of another degree of unsaturation into the newly formed ring.[6,7] To circumvent the forcing and often deleterious thermal conditions required for 4 + 2 cycloadditions involving such alkynes, several imaginative alternatives employing alkyne equivalents have been developed.[8] Among these, nitro olefins[9,10] vinyl sulfoxide,[11]

Scheme I



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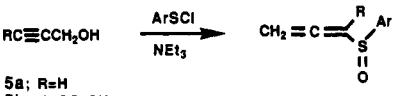
vinyl sulfones,[12,13] (*E*)- or (*Z*)-1,2-bis(phenylsulfonyl)-ethylene,[8] maleic anhydride,[14] and 1,4-benzodithiin 1,1,4,4-tetraoxide[15] are most frequently used. These acetylene equivalents are characterized by high dienophilic reactivity and by the fact that the activating group can be readily removed to introduce the second carbon–carbon double bond in the molecule.

As part of our continuing interest in the chemistry of activated allenes,[16] we investigated the use of allenic sulfoxides as propargyl alcohol synthons for cycloaddition reactions. MNDO calculations indicate that introduction of an electron-withdrawing substituent on the π-bond of allene causes a significant lowering of the LUMO energy level compared with allene itself.[16,17] The largest LUMO coefficient resides on the central carbon and the next on the position bearing the substituent group. This suggests that cycloaddition to allenic sulfoxide will proceed in a highly regioselective fashion across the activated C_1C_2 π-bond giving rise to allylic sulfoxide **2**. It is well-known that allylic sulfoxides exist in equilibrium with allylic sulfenate esters (i.e., **3**) via a 2,3-sigmatropic rearrangement.[18] Cleavage of the sulfenate ester has been accomplished using thiophilic reagents such as thiophenoxide, sodium sulfide, piperidine, or trimethyl phosphite.[19] Scheme I outlines how an allenic sulfoxide could be utilized as an *umpoled synthon* for propargyl alcohol in 4 + 2 cycloaddition chemistry. The formation of a cyclohexadiene of type **4** not only circumvents the problem of unreactivity but also avoids the low regioselectivity generally encountered with sluggish dienophiles.[20] The present paper documents the results of our investigations in this area.

Results and Discussion

The allenic sulfoxides were readily prepared from propargyl alcohol or methyl 3-hydroxy-2-butynoate (**5b**).[21] Treatment of these alcohols with the appropriate arylsulfenyl chloride and triethylamine gave rise to a transient sulfenate ester that spontaneously rearranged to the allenic sulfoxide **6**. It was important to add the triethylamine to the alkynyl alcohol at −95 °C so as to minimize side

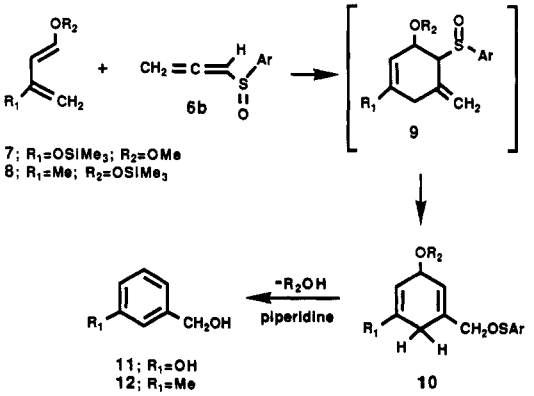


5a; R=H
5b; R=CO_2CH_3

6a; R=H; Ar=Ph
6b; R=H; Ar=2-$NO_2C_6H_4$
6c; R=H; Ar=2,4-$(NO_2)_2C_6H_3$
6d; R=CO_2CH_3; Ar=2-$NO_2C_6H_4$
6e; R=CO_2CH_3; Ar=2,4-$(NO_2)_2C_6H_3$

reactions. This, combined with a mild acid quenched at −25 °C afforded allenes of sufficient quality that no further purification was necessary. Cycloaddition reactions were conveniently monitored by the disappearance of the allene stretch (1965 cm^{-1}) in the infrared spectrum.

As our first model, we investigated the Diels–Alder reaction of (phenylsulfinyl)propadiene (**6a**) with Danishefsky's diene **7**.[22] However, all attempts to obtain a cycloadduct failed, even at elevated temperatures (150 °C) or under high pressures (6–12 kbar). This result stands in marked contrast to the Diels–Alder reaction of 1,3-dienes with (phenylsulfonyl)allene, which readily cycloadds at room temperature.[23] The difference in reactivity between the two allenes is probably a consequence of a large HOMO–LUMO gap with the (phenylsulfinyl)allene. On the basis of FMO theory,[20] introduction of electron-withdrawing groups on the aromatic ring should cause a lowering of the LUMO energy level and facilitate the cycloadditions. This indeed proved to be the case. The reaction of [(2-nitrophenyl)sulfinyl]propadiene (**6b**) with Danishefsky's diene in refluxing toluene afforded phenol **11** in



74% yield. A related reaction also occurred using 3-methyl-1-(trimethylsiloxy)-1,3-butadiene (**8**),[24] producing 3-methylbenzyl alcohol (**12**) in 81% overall yield. In both cases, the initially formed cycloadduct **9** undergoes a rapid 2,3-sigmatropic rearrangement to give **10**, which readily aromatizes under the thermal conditions. Eventual cleavage of the sulfenate affords the meta-substituted benzyl alcohol (**11** or **12**). Careful examination of the crude reaction mixture showed no signs of the para regioisomer.

The reaction of the more highly activated methyl 2-[(2-nitrophenyl)sulfinyl]-2,3-butadienoate (**6d**) with dienes **7** and **8** in methylene chloride proceeded readily at room temperature and afforded sulfenate esters **13** and **15** in over 95% yield. Treatment of the sulfenates with piperidine[25] gave rise to phthalides **14** and **16** in 85% and 88% yield, respectively.

We have also examined the reaction of allene **6b** with cyclopentadiene and found that a mixture of three cycloadducts was obtained in 35% overall yield. By conducting the reaction at 11 kbar (methylene chloride), the yield of

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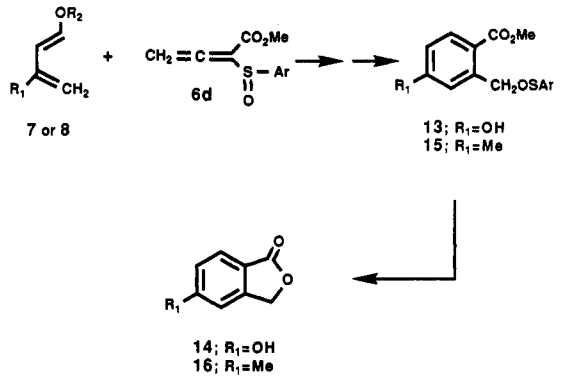
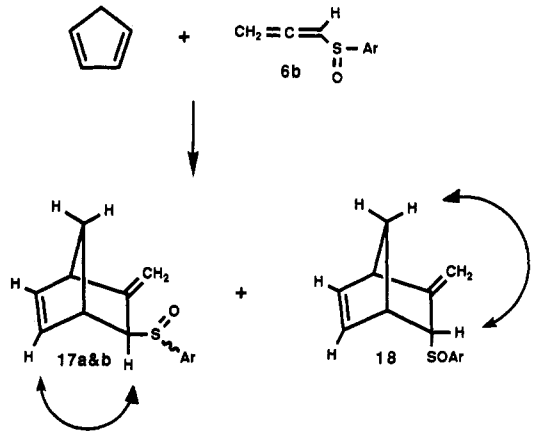


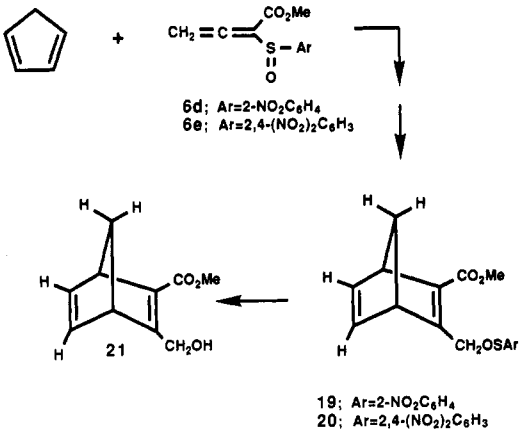
the cycloaddition increased to 85%. The stereochemical assignments of the cycloadducts follow from the two-dimensional proton–proton correlated spectra (COSY) and proximal protons (NOESY) for the three cycloadducts isolated. A key observation was that irradiation of the vinyl hydrogen resulted in NOE enhancement of the allylic hydrogen at C_6 for both exo isomers. Irradiation of the syn bridge hydrogen at C_7 resulted in NOE enhancement of the C_6 hydrogen for only the endo isomer 18.



The diasterofacial selectivity observed in the cycloaddition of vinyl sulfoxides with various dienes has received considerable attention in recent years.[26,27] The selectivity encountered has generally been explained by the preferred addition of the diene to the energetically favored s-trans (or s-cis) conformer of the vinyl sulfoxide from the less crowded side of the vinyl group (i.e., syn to the lone pair on sulfur). The conformation equilibrium of the vinyl sulfoxide is mainly imposed by the substituents present at the α- or β-position. Both dipole–dipole repulsion and steric hindrance are the dominant factors influencing the equilibrium mixture.[28,29] The low diastereoselectivity encountered in the reaction of allene **6b** with cyclopentadiene is undoubtedly a consequence of the fact that roughly equal amounts of both the s-trans and s-cis conformations are available.

Inspection of molecular models suggests that several of the cycloadducts should be able to undergo the 2,3-sigmatropic shift to the rearranged sulfenate. However, all of our attempts to induce this reaction using a variety of thiophilic reagents failed to produce the rearranged allylic alcohol. This failure is probably related to the increase in ring strain on going from the 5-methylene-2-norbornene system to the norbornadiene skeleton.[30]

An analogous set of reactions was also observed upon treating cyclopentadiene with allenes **6d** and **6e**. With these substrates, the cycloaddition occurred at room temperature and was over in several hours, producing a single adduct (**19** and/or **20**). The initially formed allylic sulfoxide undergoes a rapid 2,3-sigmatropic rearrangement, presumably as a consequence of having the double bond in conjugation with the ester functionality. Previous work in the literature has shown that the sulfenate–sulfoxide equilibrium is quite sensitive to structural effects.[31,32] Sulfenate cleavage could be accomplished using trimethyl phosphite leading to the norbornadienyl alcohol **21**. It should be point out that the reaction of methyl 4-hydroxy-2-butynoate (**5b**) with cyclopentadiene at 120 °C for 96 h or at 11 kbar for 124 h failed to give any detectable quantities of a Diels–Alder adduct. Thus, the low reactivity of **5b** can be overcome by using allene **6d** as an acetylene equivalent in Diels–Alder chemistry.



Other less reactive dienes were also found to undergo 4 + 2 cycloaddition with the (nitrophenyl)sulfinyl-activated allene **6d**. High pressures are known to markedly accelerate intermolecular cycloadditions with volumes of activation and reaction typically lying in the range of −30 to −40 $cm^3\ mol^{-1}$.[33-37] We found that the reaction of 1,3-

(30) MNDO calculations (AM1) indicate an increase in the heat of formation of i vs ii of 8 kcal/mol. The Ampac calculations also show that the conversion of iii to iv is exothermic by 1 kcal/mol.

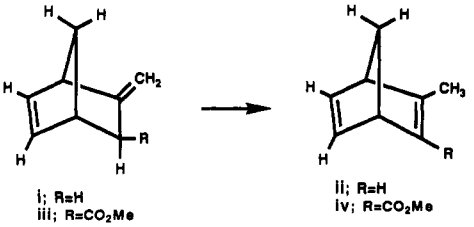


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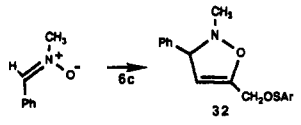
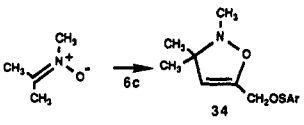
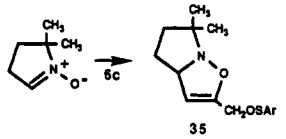
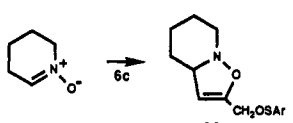
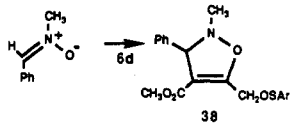
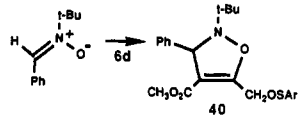
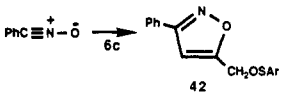
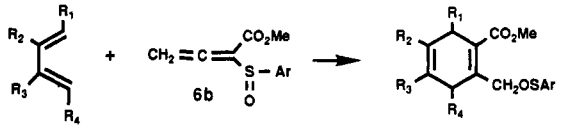
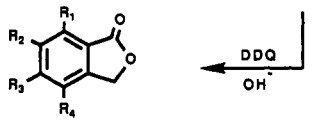
Table I

dipole	cycloadduct	dipole	cycloadduct
	32		34
	35		36
	38		40
	42		

butadiene with **6d** in methylene chloride at 25 °C under 11 kbar of pressure for 2 h afforded sulfenate **22** in 77%



22; [R_1=R_2=R_3=R_4]=H
25; [(R_1=R_4)=H; (R_2=R_3)=CH_3]
28; [(R_1=R_4)=CH_3; (R_2=R_3)=H]

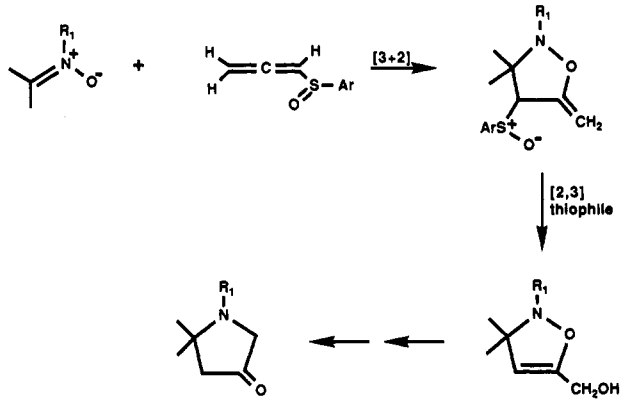


24; [R_1=R_2=R_3=R_4]=H
27; [(R_1=R_4)=H; (R_2=R_3)=CH_3]
29; [(R_1=R_4)=CH_3; (R_2=R_3)=H]
31; [(R_1=R_3)=CH_3; (R_2=R_4)=H]

isolated yield. Sulfenate ester cleavage resulted in lactonization producing dihydrophthalide **23**, which was subsequently oxidized with DDQ to phthalide **24** in 92% yield. Similar results were encountered using 2,3-dimethyl-1,3-butadiene and 2,4-hexadiene. The reaction of **6d** with 2-methyl-1,3-pentadiene was carried out so as to explore the regioselectivity of the cycloaddition. The only product formed in this case (>95% selectivity) corresponded to 5,7-dimethylphthalide **31**.

Another indication of the potential generality of [(nitrophenyl)sulfinyl]-1,2-propadiene as a propargyl alcohol synthon was provided by its reaction with a series of nitrones. Dipolar cycloaddition of nitrones with alkenes represents an efficient method for the simultaneous introduction of a nitrogen substituent and creation of a carbon–carbon bond, and this strategy has been extensively exploited for the synthesis of alkaloids possessing the pyrrolidine ring.[38,39] As part of an ongoing program in the area of heterocyclic chemistry, we have been investigating the 1,3-dipolar cycloaddition chemistry of nitrones with allenes followed by their thermal rearrangement as a method for pyrrolidine synthesis.[40-43] If the 3 + 2 cycloaddition of nitrones could be achieved with allenyl sulfoxides, then the resulting 5-methyleneisoxazolidine might undergo a 2,3-sigmatropic rearrangement and this would be followed by cleavage of the isoxazolidine ring and eventual cyclization.

In order to probe this possibility, we examined the reaction of [(2,4-dinitrophenyl)sulfinyl]propadiene (**6e**) with *N*-methyl-*C*-phenylnitrone. The reaction proceeded smoothly at 40 °C (8 h) in benzene, giving rise to the rearranged sulfenate **32**. The [(dinitrophenyl)sulfinyl]-



allene was found to react smoothly with a variety of other nitrones to give sulfenate esters as outlined in Table I. In all cases, the yield of the isolated cycloadduct is excellent. The allylic sulfenates were readily converted to the corresponding alcohols either by treatment with trimethyl phosphite or by stirring with a 10% sodium hydroxide solution. We also studied the cycloaddition reaction of allene **6e** with phenyl nitrile oxide. In this case, the isoxazole ring was formed in 90% yield. The previous results indicate that [(dinitrophenyl)sulfinyl]allene can function as a formal equivalent of propargyl alcohol, which itself is too unreactive to undergo 1,3-dipolar cycloaddition with nitrones or nitrile oxides.

Since its discovery two decades ago,[44,45] the reversible interconversion of allylic sulfenates to sulfoxides has become one of the most studied and synthetically useful 2,3-sigmatropic rearrangements known. Numerous synthetic applications of the rearrangement have been reported, including its use in the total synthesis of a variety of natural products such as steroids, prostaglandins and leukotrienes.[46] Previous work in the literature has shown that the sulfenate–sulfoxide equilibrium is quite sensitive to both solvent and structural effects.[47] The more polar the solvent, the greater the fraction of sulfoxide at equi-

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librium, which is consistent with the greater dipole moment of the sulfoxide as compared with the sulfenate.[18] The preferential formation of the sulfenate ester from the (nitroaryl)sulfinyl-substituted allenes can be attributed to the presence of the strongly electron-withdrawing nitro substituents, which destabilizes the sulfoxide functionality as a consequence of an inductive effect.[32]

In conclusion, (nitroaryl)sulfinyl-substituted allenes are conveniently prepared reagents that can serve as useful propargyl alcohol equivalents in both Diels–Alder and 1,3-dipolar cycloaddition reactions. The dienophilic reactivity of the allenyl sulfoxide is much greater than that of the corresponding alkyne. The use of these propargyl alcohol equivalents avoids the low regioselectivity encountered with alkynes in the 4 + 2 cycloaddition reaction. The initially formed cycloadducts readily undergo a 2,3-sigmatropic rearrangement to produce stable sulfenate esters that can be easily cleaved with thiophilic reagents.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra nitrogen. Flash silica gel chromatography was used to separate and purify the crude reaction mixtures.

General Allene Preparation. An oven-dried three-neck round-bottom flask equipped with a pressure-equalized dropping funnel was charged with a 0.25 M solution of the appropriate propargyl alcohol in methylene chloride. This solution was cooled to −95 °C, and then 1 equiv of triethylamine was added. The mixture was stirred for 10 min, and a 1 M solution of the appropriate sulfenyl chloride (1 equiv) in methylene chloride was added dropwise. Stirring was continued at −95 °C for 10 min, and the bath was allowed to slowly warm to −25 °C and was then quenched with a 1% aqueous hydrochloric acid solution. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The combined organic extracts were washed with water and brine and dried over anhydrous sodium sulfate. Concentration of the solution under reduced pressure afforded the appropriate allene.

(Phenylsulfinyl)-1,2-propadiene (6a). By use of the previous procedure, 3.23 g (57.7 mmol) of propargyl alcohol, 8.02 g of benzenesulfenyl chloride (50 mmol), and 5.61 g of triethylamine (40 mmol) afforded (phenylsulfinyl)-1,2-propadiene (**6a**) in 93% yield as a pale yellow oil:[48] IR (neat) 3060, 2990, 1935, 1440, 1085, 860, 745, and 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 5.29 (d, 2 H, J = 6.3 Hz), 6.07 (t, 1 H, J = 6.3 Hz), and 7.45–7.66 (m, 5 H).

[(2-Nitrophenyl)sulfinyl]-1,2-propadiene (6b). By use of the previous procedure, 976 mg of propargyl alcohol (17.4 mmol), 1.76 g of triethylamine (30 mmol), and 3.0 g (11 mmol) of 2-nitrobenzenesulfenyl chloride afforded [(2-nitrophenyl)-sulfinyl]-1,2-propadiene (**6b**) in 80% yield as a yellow solid: mp 83–84 °C; IR (KBr) 3060, 3000, 1950, 1520, 1330, 1310, 1070, and 1030 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 5.25 (dd, 1 H, J = 13, and 6 Hz), 5.35 (dd, 1 H, J = 13 and 6 Hz), 6.32 (t, 1 H, J = 6 Hz), 7.72 (t, 1 H, J = 7 Hz), 7.95 (t, 1 H, J = 7 Hz), 8.25 (d, 1 H, J = 7 Hz), and 8.30 (d, 1 H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 82.1, 101.3, 125.2, 126.4, 131.2, 135.3, 143.1, 144.0, and 208.1. Anal. Calcd for $C_9H_7NO_3S$: C, 51.67; H, 3.38; N, 6.70. Found: C, 51.59; H, 3.36; N, 6.59.

[(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). By use of the previous procedure, 788 mg of propargyl alcohol (14 mmol), 1.4 g of triethylamine (10 mmol), and 3.0 g of 2,4-dinitrobenzenesulfenyl chloride (14 mmol) afforded [(2,4-dinitrophenyl)sulfinyl]-1,2-propadiene (**6c**) in 85% yield: IR (KBr) 3060, 3000, 1950, 1520, 1330, 1310, 1070, and 1030 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 5.31 (dd, 1 H, J = 13 and 6 Hz), 5.54 (dd, 1 H, J = 13 and 6 Hz), 6.35 (t, 1 H, J = 6 Hz), 8.52 (d, 1 H, J = 9 Hz), 8.82 (dd, 1 H, J = 9 and 3 Hz), and 9.16 (d, 1 H, J = 3 Hz); ^{13}C NMR ($CDCl_3$) δ 82.1, 101.6, 120.7, 129.3, 130.2, 145.1, 149.2, 151.3, and 208.5; UV (95% ethanol) λ_{max} 238 nm (ϵ 11 650). Anal. Calcd for $C_9H_6N_2O_5S$: C, 42.52; H, 2.38; N, 11.03. Found: C, 42.46; H, 2.31; N, 10.97.

Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d). By use of the previous procedure, 2.0 g (17.5 mmol) of methyl 4-hydroxy-2-butynoate (**1b**),[21] 2.44 mL of triethylamine (17.5 mmol), and 3.0 g of 2-nitrobenzenesulfenyl chloride (16 mmol) afforded methyl 2-[(2-nitrophenyl)sulfinyl]-2,3-butadienoate (**6d**) in 85% yield as a yellow solid: mp 99–100 °C; IR ($CHCl_3$) 3090, 3020, 2970, 1965, 1730, 1535, 1430, 1340, 1280, 1080, 1045, and 860 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.86 (s, 3 H), 5.02 (d, 1 H, J = 15.8 Hz), 5.24 (d, 1 H, J = 15.8 Hz), 7.71 (m, 1 H), 7.96 (m, 1 H), and 8.29 (m, 1 H). Anal. Calcd for $C_{11}H_9NO_5S$: C, 49.44; H, 3.39; N, 5.24. Found: C, 49.15; H, 3.55; N, 5.13.

Methyl 2-[(2,4-Dinitrophenyl)sulfinyl]-2,3-butadienoate (6e). By use of the previous procedure, 2.0 g (17.5 mmol) of methyl 4-hydroxy-2-butynoate (**1b**),[21] 2.44 mL of triethylamine (17.5 mmol), and 3.73 g (15.9 mmol) and 2,4-dinitrobenzenesulfenyl chloride afforded methyl 2-[(2,4-dinitrophenyl)sulfinyl]-2,3-butadienoate (**6e**) in 90% yield as a yellow solid: mp 127–128 °C; IR ($CHCl_3$) 3120, 3040, 2940, 1965, 1730, 1545, 1350, 1290, 1270, 1095, and 840 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.89 (s, 3 H), 5.21 (d, 1 H, J = 16.0 Hz), 5.44 (d, 1 H, J = 16.0 Hz), 8.58 (d, 1 H, J = 8.6 Hz), 8.77 (dd, 1 H, J = 8.6 and 2.2 Hz), and 9.12 (d, 1 H, J = 2.2 Hz). Anal. Calcd for $C_{11}H_8N_2O_7S$: C, 42.31; H, 2.58; N, 8.97. Found: C, 42.44, H, 2.75; N, 8.88.

Reaction of [(2-Nitrophenyl)sulfinyl]-1,2-propadiene (6b) with Danishefsky's Diene. A solution containing 250 mg (1 mmol) of allene **6b** and 1.1 mL (1.5 mmol) of Danishefsky's diene[22] in 5 mL of dry toluene was heated at 110 °C for 12 h. The solution was cooled to room temperature and was concentrated under reduced pressure. Purification by chromatography afforded (3-hydroxyphenyl)methyl 2-nitrobenzenesulfenate as a yellow oil in 78% yield: IR ($CHCl_3$) 3300, 2960, 2930, 2850, 1590, 1505, 1330, 1260, 1100, and 1010 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.84 (s, 2 H), 4.98 (br s, 1 H), 6.83 (dd, 1 H, J = 7.8 and 2.3 Hz), 6.92 (d, 1 H, J = 2.3 Hz), 6.96 (d, 1 H, J = 7.8 Hz), 7.23–7.35 (m, 2 H), 7.70 (dd, 1 H, J = 7.4 and 1.3 Hz), 7.77 (dd, 1 H, J = 8.3 and 1.3 Hz), and 8.30 (dd, 1 H, J = 8.3 and 1.3 Hz). This material was taken up in 10 mL of acetonitrile and was treated with 5 equiv of piperidine. The solution was stirred at room temperature for 2 h and was then concentrated under reduced pressure. Chromatography gave 3-hydroxybenzyl alcohol (**11**) in 74% yield as a white crystalline solid: mp 68–69 °C; IR (KBr) 3360, 3090, 2740, 1620, 1590, 1490, 1410, 1270, 1150, 970, and 780 cm^{-1}; NMR (CD_3CN, 300 MHz) δ 3.15 (br s, 1 H), 4.40 (s, 2 H), 6.66 (dd, 1 H, J = 7.9 and 2.4 Hz), 6.75–6.80 (m, 2 H), and 7.13 (t, 1 H, J = 7.9 Hz). Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.55.

Reaction of [(2-Nitrophenyl)sulfinyl]-1,2-propadiene (6b) with 3-Methyl-1-(trimethylsiloxy)-1,3-butadiene. By use of the same procedure as outlined previously, 300 mg of allene **6b** and 1.1 g of 3-methyl-1-(trimethylsiloxy)-1,3-butadiene[24] afforded (3-methylphenyl)methyl 2-nitrobenzenesulfenate as a yellow oil in 83% yield: IR (neat) 3040, 2930, 2880, 1600, 1570, 1505, 1450, 1340, 1310, and 740 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.38 (s, 3 H), 4.86 (s, 2 H), 7.17–7.32 (m, 5 H), 7.69 (t, 1 H, J = 7.7 Hz), 7.79 (d, 1 H, J = 8.0 Hz), and 8.30 (d, 1 H, J = 8.0 Hz). This material was subjected to sulfenate ester cleavage as previously described. A mixture containing 150 mg of the above material and 0.27 mL of piperidine gave 3-methylbenzyl alcohol (**12**) in 81% yield as a colorless oil: IR (neat) 3400, 3060, 2960, 2900, 1620, 1420, 1360, 1165, 1050, 860, and 710 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.72 (t, 1 H, J = 5.6 Hz), 2.36 (s, 3 H), 4.65 (d, 2 H, J = 5.6 Hz), 7.09–7.18 (m, 5 H), and 7.22–7.27 (m, 1 H). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.77; H, 8.22.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with Danishefsky's Diene. To a solution containing 300 mg of allene **6d** in 5 mL of methylene chloride at 0 °C was added 0.33 mL of Danishefsky's diene. The solution was allowed to warm to room temperature and was stirred for 12 h. Concentration of the solvent under reduced pressure afforded (2-carbomethoxy-5-hydroxyphenyl)methyl 2-nitrobenzenesulfonate (**13**) in quantitative yield as a yellow crystalline solid: mp 106–107 °C; IR (KBr) 3420, 3040, 2940, 1735, 1690, 1580, 1510, 1390, 900, and 745 cm^{-1}; NMR (DMSO-d_6, 300 MHz) δ 3.69 (s, 3 H), 4.09 (s, 1 H), 5.24 (s, 2 H), 6.78 (dd, 1 H, J = 8.4 and 1.8

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Hz), 7.45 (t, 1 H, J = 7.5 Hz), 7.75–7.88 (m, 3 H), and 8.32 (d, 1 H, J = 8.4 Hz). This material was taken up in 10 mL of acetonitrile and was treated with 0.56 mL of piperidine. The solution was allowed to stir at room temperature for 2 h and was then concentrated under reduced pressure. Purification gave 5-hydroxyphthalide (14) as a white crystalline solid in 85% yield: mp 222–223 °C (lit.[49] mp 223–224 °C); IR (KBr) 3280, 2930, 1730, 1610, 1470, 1275, 1100, 1070, 1005, and 610 cm^{-1}; NMR (DMSO-d_6, 300 MHz) δ 5.21 (s, 2 H), 6.87–6.90 (m, 2 H), 7.60 (d, 1 H, J = 9.0 Hz), and 10.60 (s, 1 H). Anal. Calcd for $C_8H_6O_3$: C, 64.00; H, 4.03. Found: C, 64.13; H, 4.07.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with 3-Methyl-1-(trimethylsiloxy)-1,3-butadiene. A solution containing 300 mg of allene **6d** and 260 mg of 3-methyl-1-(trimethylsiloxy)-1,3-butadiene[24] in 10 mL of methylene chloride was stirred at room temperature for 12 h. The solution was concentrated under reduced pressure and was chromatographed to give (2-carbomethoxy-5-methylphenyl)methyl 2-nitrobenzenesulfenate (15) in 93% yield as a yellow oil: IR ($CHCl_3$) 3040, 2970, 1720, 1510, 1340, 1310, 1280, 1095, 985, and 830 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.46 (s, 3 H), 3.84 (s, 3 H), 5.35 (s, 2 H), 7.19–7.32 (m, 2 H), 7.55 (s, 1 H), 7.69 (t, 1 H, J = 7.9 Hz), 7.81 (d, 1 H, J = 8.3 Hz), 7.92 (d, 1 H, J = 7.9 Hz), and 8.30 (d, 1 H, J = 8.3 Hz). This material was subjected to sulfenate ester cleavage as previously described to give 5-methylphthalide (16) as a white crystalline solid in 88% yield: mp 119–120 °C (lit.[50] mp 116–117 °C); IR ($CHCl_3$) 3030, 2950, 1755, 1630, 1350, 1120, 1050, 1015, 835, and 680 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.48 (s, 3 H), 5.26 (s, 2 H), 7.27 (s, 1 H), 7.33 (d, 1 H, J = 7.8 Hz), and 7.80 (d, 1 H, J = 7.8 Hz). Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.99; H, 5.46.

Reaction of [(2-Nitrophenyl)sulfinyl]-1,2-propadiene (6b) with Cyclopentadiene. A solution containing 0.47 g of freshly prepared cyclopentadiene and 300 mg of allene **6b** in 6.5 mL of methylene chloride was sealed in a 7 mL polypropylene vial, and this was pressurized at 23 °C for 8 h at 11 kbar. The solvent was removed under reduced pressure, and the resulting residue was subjected to silica gel flash chromatography using a 25% ethyl acetate–hexane mixture as the eluent to give a mixture of diastereomeric cycloadducts. The first fraction isolated was identified as *exo*-5-methylene-6-[(2-nitrophenyl)sulfinyl]bicyclo[2.2.1]-hept-2-ene (17a) in 30% yield as a yellow oil: IR ($CHCl_3$) 3020, 1535, 1350, 1070, 1040, 900, and 860 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.65 (d, 1 H, J = 8.7 Hz), 2.29 (d, 1 H, J = 8.7 Hz), 3.02 (br s, 1 H), 3.26 (m, 1 H), 3.33 (br s, 1 H), 5.26 (br s, 1 H), 5.35 (br s, 1 H), 6.02 (dd, 1 H, J = 5.3 and 3.1 Hz), 6.33 (dd, 1 H, J = 5.3 and 3.1 Hz), 7.73 (t, 1 H, J = 7.6 Hz), 7.98 (t, 1 H, J = 7.6 Hz), and 8.38 (t, 2 H, J = 7.6 Hz); HRMS calcd for $C_{14}H_{13}NO_3S$ 275.0615, found 275.0606.

The second fraction (15%) contained *exo*-5-methylene-6-[(2-nitrophenyl)sulfinyl]bicyclo[2.2.1]hept-2-ene (17b): mp 95–96 °C; IR ($CHCl_3$) 3015, 1535, 1350, 1070, 1045, 910, and 860 cm^{-1}; NMR ($CDCl_3$) δ 1.84 (d, 1 H, J = 8.8 Hz), 2.30 (d, 1 H, J = 8.8 Hz), 3.30 (br s, 1 H), 3.37 (br s, 1 H), 3.46 (br s, 1 H), 4.32 (s, 1 H), 5.20 (s, 1 H), 6.18 (dd, 1 H, J = 5.2 and 3.0 Hz), 6.29 (dd, 1 H, J = 5.2 and 3.0 Hz), 7.71 (t, 1 H, J = 7.7 Hz), 7.94 (t, 1 H, J = 7.7 Hz), 8.28 (d, 1 H, J = 8.0 Hz), and 8.34 (d, 1 H, J = 8.0 Hz). Anal. Calcd for $C_{14}H_9NO_5S$: C, 61.08; H, 4.76; N, 5.09. Found: C, 61.20; H, 4.79; N, 5.05.

The third fraction (40%) contained *endo*-5-methylene-6-[(2-nitrophenyl)sulfinyl]bicyclo[2.2.1]hept-2-ene (18): mp 105–106 °C; IR ($CHCl_3$) 3000, 1530, 1345, 1070, 1040, 910, and 850 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.43 (d, 1 H, J = 8.7 Hz), 1.67 (dt, 1 H, J = 8.7 and 1.8 Hz), 3.04 (br s, 1 H), 3.34 (br s, 1 H), 3.84 (m, 1 H), 4.79 (d, 1 H, J = 2.0 Hz), 5.09 (d, 1 H, J = 2.0 Hz), 6.18 (dd, 1 H, J = 5.5 and 2.9 Hz), 6.55 (dd, 1 H, J = 5.5 and 2.9 Hz), 7.67 (td, 1 H, J = 10.2 and 1.4 Hz), 7.96 (td, 1 H, J = 10.2 and 1.2 Hz), 8.32 (dd, 1 H, J = 8.0 and 1.2 Hz), and 8.37 (dd, 1 H, J = 8.0 and 1.4 Hz). Anal. Calcd for $C_{14}H_9NO_5S$: C, 61.08; H, 4.76; N, 5.09. Found: C, 61.18; H, 4.77; N, 5.01.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with Cyclopentadiene. A solution containing 124 mg (1.87 mmol) of freshly prepared cyclopentadiene and 250 mg of allene **6d** (0.94 mmol) in 5 mL of methylene chloride was stirred at room temperature for 8 h. Removal of the solvent under reduced pressure left a yellow oil that was purified to give 2-carbomethoxy-3-[[(2-nitrophenyl)sulfenyloxy]methyl]bicyclo-[2.2.1]hepta-2,5-diene (19) as a pale yellow oil in 93% yield: IR (neat) 3090, 3000, 2975, 2880, 1705, 1510, 1340, 1305, 1240, 1105, and 735 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.09 (d, 1 H, J = 6.6 Hz), 2.18 (d, 1 H, J = 6.6 Hz), 3.66 (s, 3 H), 3.96 (s, 2 H), 4.84 (d, 1 H, J = 13.8 Hz), 5.07 (d, 1 H, J = 13.8 Hz), 6.86–6.93 (m, 2 H), 7.27–7.33 (m, 2 H), 7.70–7.73 (m, 1 H), and 8.29 (d, 1 H, J = 8.2 Hz). This material was taken up in 50 mL of methanol, and the solution was treated with 0.22 mL (1.87 mmol) of trimethyl phosphite. The mixture was stirred at room temperature for 12 h, the solvent was removed under reduced pressure, and the residue was taken up in ether. The ethereal solution was washed with a saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified to give 2-carbomethoxy-3-(hydroxymethyl)bicyclo[2.2.1]hepta-2,5-diene (21) as a colorless oil in 82% yield: IR (neat) 3440, 3020, 2960, 2890, 1715, 1630, 1445, 1300, 1250, 1075, and 790 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.00 (d, 1 H, J = 6.6 Hz), 2.13 (d, 1 H, J = 6.6 Hz), 3.56 (s, 1 H), 3.77 (s, 3 H), 3.93 (s, 1 H), 4.52 (dd, 1 H, J = 16.5 and 4.7 Hz), 4.60 (t, 1 H, J = 4.7 Hz), 4.69 (dd, 1 H, J = 16.5 and 4.7 Hz), 6.74 (dd, 1 H, J = 4.9 and 3.3 Hz), and 6.90 (dd, 1 H, J = 4.9 and 3.3 Hz); HRMS calcd for $C_{10}H_{12}O_3$ 180.0789, found 180.0786.

A similar transformation was encountered from the reaction of methyl 2-[(2,4-dinitrophenyl)sulfenyloxy]-2,3-butadienoate (6e) with cyclopentadiene. The major material formed (95%) corresponded to 2-carbomethoxy-3-[[(2,4-dinitrophenyl)sulfinyl]-methyl]bicyclo[2.2.1]hepta-2,5-diene (20): IR ($CHCl_3$) 3115, 2960, 1710, 1605, 1525, 1340, 1310, 1300, 925, and 835 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.14 (d, 1 H, J = 6.6 Hz), 2.21 (d, 1 H, J = 6.6 Hz), 3.70 (s, 3 H), 3.94 (s, 1 H), 3.99 (s, 1 H), 4.92 (d, 1 H, J = 13.2), 5.12 (d, 1 H, J = 13.2), 6.88–6.92 (m, 2 H), 7.92 (d, 1 H, J = 9.1 Hz), 8.50 (dd, 1 H, J = 9.1 and 2.3 Hz), and 9.13 (d, 1 H, J = 2.3 Hz). This material was converted to 2-carbomethoxy-3-(hydroxymethyl)bicyclo[2.2.1]hepta-2,5-diene (21) in 68% yield using the procedure outlined previously for sulfenate 19.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with 1,3-Butadiene. A solution containing 250 mg of allene **6d** in 2 mL of methylene chloride was added to 5 mL of methylene chloride that contained 1.0 g of 1,3-butadiene at −78 °C. The solution was transferred to a 7-mL polypropylene vial, and this was pressurized to 11 kbar at 23 °C for 2 h. Concentration of the solution under reduced pressure afforded a yellow oil that was purified to give (2-carbomethoxy-1,4-cyclohexadienyl)methyl 2-nitrobenzenesulfenate (22; 77% yield): IR ($CHCl_3$) 3035, 2980, 2940, 2880, 1745, 1705, 1205, 1110, 1035, 1010, 960, and 810 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.96–3.12 (m, 2 H), 3.68 (s, 3 H), 4.86 (s, 2 H), 5.74 (s, 2 H), 7.31 (ddd, 1 H, J = 8.3, 6.9 and 1.5 Hz), 7.80–7.69 (m, 1 H), and 8.29 (dd, 1 H, J = 8.3 and 0.9 Hz).

This material was subjected to sulfenate ester cleavage as previously described to give 4,7-dihydrophthalide (23; 75%) as a crystalline solid:[51] mp 58–59 °C; IR ($CHCl_3$) 3040, 2900, 1760, 1700, 1640, 1255, 1040, 1015, 965, and 630 cm^{-1}; NMR ($CHCl_3$, 300 MHz) δ 2.85–2.93 (m, 2 H), 2.99–3.05 (m, 2 H), 4.73–4.75 (m, 2 H), 5.74–5.81 (m, 1 H), and 5.85–5.91 (m, 1 H). Anal. Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92. Found: C, 70.33; H, 5.81.

A solution containing 170 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 100 mg of 4,7-dihydrophthalide (23) in 10 mL of toluene was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the resulting residue was subjected to flash silica gel chromatography using a 20% ethyl acetate–hexane mixture as the eluent to give a colorless oil that crystallized on standing to give phthalide 24 in 92% yield:[51] mp 72–73 °C; IR ($CHCl_3$) 3040, 2960, 2895, 1760, 1625, 1480, 1300, 1050, 1010, and 685 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 5.31 (s, 2 H), 7.47–7.55 (m, 2 H), 7.67 (dt, 1 H, J = 7.6 and 1.1 Hz), and 7.91 (d, 1 H, J = 7.6 Hz). Anal. Calcd for $C_8H_6O_2$: C, 71.64; H, 4.51. Found: C, 71.71; H, 4.56.

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Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with 2,3-Dimethyl-1,3-butadiene. A solution containing 0.53 mL of 2,3-dimethyl-1,3-butadiene and 250 mg of allene **6d** in 7 mL of methylene chloride was sealed in a 7-mL polypropylene vial, and this was pressurized at 23 °C for 2 h at 10 kbar. At the end of this time, the solvent was removed under reduced pressure and the resulting residue was purified to give (2-carbomethoxy-4,5-dimethyl-1,4-cyclohexadienyl)methyl 2-nitrobenzenesulfenate (**25**) in 78% yield as a pale yellow oil: IR ($CHCl_3$) 3010, 2940, 2780, 1715, 1510, 1340, 1310, 1280, 1000, and 965 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.68 (s, 3 H), 1.71 (s, 3 H), 2.89–2.94 (m, 2 H), 3.00–3.05 (m, 2 H), 3.68 (s, 3 H), 4.88 (m, 2 H), 7.32 (ddd, 1 H, J = 8.4, 7.0 and 1.3 Hz), 7.69–7.81 (m, 2 H), and 8.30 (dd, 1 H, J = 8.4 and 1.3 Hz).

This material was subjected to sulfenate ester cleavage as previously described to give 5,6-dimethyl-4,7-dihydrophthalide (**26**) in 86% yield as a crystalline solid:[52] mp 122–123 °C; IR ($CHCl_3$) 3010, 2930, 2870, 1745, 1700, 1440, 1290, 1165, 1070, and 1015 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.74 (s, 6 H), 2.80–2.83 (m, 2 H), 2.90–2.95 (m, 2 H), and 4.71–4.73 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.0, 18.2, 27.5, 31.1, 70.9, 120.2, 122.8, 123.9, 157.7 and 172.9. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36. Found: C, 73.31; H, 7.40.

This material was subjected to DDQ oxidation as previously described to give 5,6-dimethylphthalide (**27**) as a crystalline solid:[53] mp 115–116 °C; IR ($CHCl_3$) 3040, 2960, 1765, 1360, 1120, 1040, 1015, 995, and 880 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.36 (s, 3 H), 2.38 (s, 3 H), 5.24 (s, 2 H), 7.24 (s, 1 H), and 7.67 (s, 1 H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.80; H, 6.34.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with *trans,trans*-2,4-Hexadiene. A solution containing 1.0 mL of *trans,trans*-2,4-hexadiene and 250 mg of allene **6d** in 7 mL of methylene chloride was sealed in a 7-mL polypropylene vial, and this was pressurized at 23 °C for 2 h at 11 kbar. The solvent was removed under reduced pressure, and the resulting residue was subjected to flash silica gel chromatography using a 20% ethyl acetate–hexane mixture as the eluent to give (2-carbomethoxy-3,6-dimethyl-1,4-cyclohexadienyl)methyl 2-nitrobenzenesulfenate (**28**; 88% yield) as a pale yellow oil: IR ($CHCl_3$) 2980, 2940, 2880, 1715, 1510, 1345, 1310, 1270, 1250, 960, and 860 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.09 (d, 3 H, J = 6.9 Hz), 1.24 (d, 3 H, J = 6.9 Hz), 3.16–3.29 (m, 2 H), 3.71 (s, 3 H), 4.65 (d, 1 H, J = 12.7 Hz), 4.85 (d, 1 H, J = 12.7 Hz), 5.68–5.69 (m, 2 H), 7.28–7.33 (m, 1 H), 7.67–7.76 (m, 2 H), and 8.28–8.31 (m, 1 H).

This material was subjected to sulfenate ester cleavage as previously described to give *cis*-4,7-dimethyl-4,7-dihydrophthalide (**29**) in 85% yield as a white crystalline solid:[54] mp 114–115 °C; IR ($CHCl_3$) 3040, 2990, 2950, 2880, 1755, 1695, 1460, 1355, 1250, 1040, and 900 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.19 (d, 3 H, J = 7.0 Hz), 1.22 (d, 3 H, J = 7.0 Hz), 2.98–3.14 (m, 2 H), 4.63 (ddd, 1 H, J = 16.9, 2.3 and 1.1 Hz), 4.79 (dd, 1 H, J = 16.9 and 1.1 Hz), 5.57 (ddd, 1 H, J = 10.0, 3.1 and 1.5 Hz), and 5.68 (ddd, 1 H, J = 10.0, 3.1 and 1.5 Hz). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36. Found: C, 73.05; H, 7.37.

This material was subjected to DDQ oxidation as previously described to give 4,7-dimethylphthalide (**30**) as a crystalline solid: mp 87–88 °C (lit.[55] mp 87–88 °C); IR ($CHCl_3$) 3030, 2940, 2860, 1760, 1250, 1095, 1045, and 830 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3 H), 2.63 (s, 3 H), 5.16 (s, 2 H), 7.16 (d, 1 H, J = 7.6 Hz), and 7.29 (d, 1 H, J = 7.6 Hz). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.95; H, 6.29.

Preparation of 5,7-Dimethylphthalide (31). A solution containing 300 mg of allene **6d** and 461 mg of *trans*-2-methyl-1,3-pentadiene in 7 mL of methylene chloride was sealed in a polypropylene vial, and this was pressurized at 23 °C for 4 h at 12 kbar. The resulting solution was filtered through a small plug of silica gel, and the solvent was removed under reduced pressure to leave behind a yellow oil. This material was suspended in 50 mL of methanol and was treated with 280 mg of trimethyl phosphite. Stirring was continued at room temperature for 4 h, at which time 50 mL of a saturated sodium bicarbonate solution was added. The resulting suspension was stirred for 30 min, extracted with ether, washed with water and brine, and dried over sodium sulfate. The solvent was removed under reduced pressure, and the crude residue was dissolved in 10 mL of toluene that contained 226 mg of 2,3-dichloro-5,6-dicyanoquinone. The mixture was heated at 110 °C for 12 h and was then allowed to cool to 25 °C. The solvent was removed under reduced pressure, and the resulting residue was purified to give 5,7-dimethylphthalide (**31**) as a white crystalline solid in 63% yield: mp 94–95 °C (lit.[50] mp 95–96 °C); IR ($CHCl_3$) 3040, 1755, 1620, 1365, 1045, 1025, 870, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.41 (s, 3 H), 2.62 (s, 3 H), 5.18 (s, 2 H), and 7.04–7.06 (m, 2 H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.03; H, 6.25.

Cycloaddition of *N*-Methyl-*C*-phenylnitrone with [(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). A solution containing 625 mg of allene **6c** and 405 mg of *N*-methyl-*C*-phenylnitrone[56] in 5 mL of benzene was placed in a sealed tube, and the mixture was heated at 50 °C for 12 h. The solution was passed through a short column of silica gel using a 30% chloroform–hexane mixture as the eluent. The NMR spectrum of the residue showed that it corresponded to 5-[[(2,4-dinitrophenyl)-sulfenyloxy]methyl]-2-methyl-3-phenyl-Δ^4-isoxazoline (**32**): IR (neat) 1600, 1520, 1450, 1330, and 1300 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.92 (s, 3 H), 4.52 (d, 1 H, J = 13 Hz), 4.58 (d, 1 H, J = 13 Hz), 4.75 (d, 1 H, J = 2 Hz), 5.21 (d, 1 H, J = 2 Hz), 7.25 (m, 5 H), 8.05 (d, 1 H, J = 9 Hz), 8.42 (dd, 1 H, J = 9 and 2 Hz), and 9.07 (d, 1 H, J = 2 Hz).

The labile sulfenate ester **32** was not purified but instead was hydrolyzed to the corresponding alcohol as follows. To a solution containing 414 mg of sulfenate ester **32** in 10 mL of methanol was added 248 mg of trimethyl phosphite, and the mixture was heated at 60 °C for 20 h. Concentration of the solution under reduced pressure afforded a brown oil that was purified by silica gel chromatography using a 20% ethyl acetate–hexane mixture as the eluent. The major fraction (150 mg, 82% yield) contained 5-(hydroxymethyl)-2-methyl-3-phenyl-Δ^4-isoxazoline (**33**) as a pale yellow oil: IR (neat) 3400, 1600, 1520, 1450, and 1340 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 2.81 (s, 3 H), 4.23 (s, 2 H), 4.65 (d, 1 H, J = 3 Hz), 4.93 (d, 1 H, J = 3 Hz), and 7.35 (s, 5 H); HRMS calcd for $C_{11}H_{13}NO_2$ 191.0846, found 191.0842.

Cycloaddition of *C,C*-Dimethyl-*N*-methylnitrone with [(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). A solution containing 174 mg of *C,C*-dimethyl-*N*-methylnitrone[57] and 508 mg of allene **6c** in 10 mL of methylene chloride was heated at 50 °C for 4 h. Concentration of the solution under reduced pressure afforded 668 mg of 5-[[(2,4-dinitrophenyl)sulfenyl-oxy]methyl]-2-methyl-3-phenyl-Δ^4-isoxazoline (**34**; 98% yield) as a yellow oil: IR (neat) 3100, 3000, 2910, 2820, 1600, 1520, 1450, 1340, 1300, 1230, 1150, 1090, and 1050 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.21 (s, 6 H), 2.65 (s, 3 H), 4.47 (s, 2 H), 5.02 (s, 1 H), 8.08 (d, 1 H, J = 9 Hz), 8.45 (dd, 1 H, J = 9 and 3 Hz), and 9.13 (d, 1 H, J = 3 Hz); HRMS calcd for $C_{18}H_{15}N_3O_6S$ 341.0681, found 341.0673.

Cycloaddition of 5,5-Dimethyl-1-pyrroline *N*-Oxide with [(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). A solution containing 339 mg of 5,5-dimethyl-1-pyrroline *N*-oxide and 635 mg of allene **6c** in 10 mL of benzene was heated in a sealed tube at 50 °C for 10 h. The dark solution was passed through a short column of silica gel using a 50% chloroform–hexane mixture as the eluent. The major fraction (870 mg, 95% yield) was a clear oil whose structure corresponded to 5,5-dimethyl-2-[[(2,4-dinitrophenyl)sulfenyloxy]methyl]-3a,4,5,6-tetrahydro-2*H*-pyrrolo[1,2-*b*]oxazole (**35**): IR (neat) 3100, 3000, 2880, 2790, 1600, 1520, 1460, 1340, 1300, 1230, 1150, 1090, and 1050 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.21 (s, 3 H), 1.40 (s, 3 H), 1.32 (m, 2 H), 1.73 (m, 2 H), 4.56 (s, 2 H), 4.71 (m, 1 H), 5.17 (d, 1 H, J = 3 Hz), 8.24 (d, 1 H, J = 9 Hz), 8.73 (dd, 1 H, J = 9 and 3 Hz), and 9.26 (d, 1 H, J = 3 Hz); HRMS calcd for $C_{15}H_{17}N_3O_6S$ 367.0838, found 367.0837.

Cycloaddition of 3,4,5,6-Tetrahydropyridine *N*-Oxide with [(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). A methylene chloride solution of 3,4,5,6-tetrahydropyridine *N*-oxide[58]

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was prepared by stirring 500 mg of *N*-hydroxypiperidine in 30 mL of methylene chloride with 2.6 g of mercuric oxide for 20 min. The mixture was filtered through a Celite pad. This mixture was added to a solution containing 762 mg of allene **6c** in 20 mL of methylene chloride, and the solution was stirred at 25 °C for 12 h, after which the solvent was removed under reduced pressure. The resulting residue was purified to give 2-[[(2,4-dinitrophenyl)sulfenyloxy]methyl]-4,5,6,7-tetrahydro-3a*H*-isoxazolo-[2,3-*a*]pyridine (**36**; 950 mg, 95% yield) as a yellow oil: IR (CCl_4) 1600, 1530, 1340, and 1310 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.62 (m, 6 H), 3.02 (m, 2 H), 4.41 (m, 1 H), 4.45 (d, 1 H, J = 12 Hz), 4.47 (d, 1 H, J = 12 Hz), 5.16 (s, 1 H), 8.04 (d, 1 H, J = 9 Hz), 8.45 (dd, 1 H, J = 9 and 2 Hz), and 9.05 (d, 1 H, J = 2 Hz).

To a solution containing 500 mg of sulfenate ester **36** in 100 mL of tetrahydrofuran was added 75 mL of a 10% aqueous sodium hydroxide solution. The dark solution was stirred at 25 °C for 1 h, and the solvent was removed under reduced pressure. The resulting aqueous solution was poured into 100 mL of methylene chloride. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 170 mg (77% yield) of an oil whose structure was assigned as 2-(hydroxymethyl)-4,5,6,7-tetrahydro-3a*H*-isoxazolo[2,3-*a*]pyridine (**37**) on the basis of its spectral properties: IR (neat) 3300 (br), 2950, 2860, 1610, 1535, 1450, 1360, 1070, 915, and 750 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.60 (m, 4 H), 1.90 (m, 2 H), 3.15 (m, 2 H), 3.65 (br s, 1 H), 4.30 (s, 2 H), 4.40 (m, 1 H), and 4.95 (s, 1 H). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.02. Found: C, 61.86, H, 8.44; N, 8.86.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with *N*-Methyl-*C*-phenylnitrone. A solution containing 139 mg of *N*-methyl-*C*-phenylnitrone[56] (1.02 mmol) and 250 mg of allene **6d** (0.94 mmol) in 5 mL of methylene chloride was stirred at 0 °C for 30 min. Removal of the solvent under reduced pressure left a yellow oil that was purified to give 4-carbomethoxy-5-[[(2,4-dinitrophenyl)sulfenyloxy]methyl]-2-methyl-3-phenyl-Δ^4-isoxazoline (**38**) as a pale yellow oil in 86% yield: IR ($CHCl_3$) 3040, 3015, 1705, 1665, 1510, 1310, 1190, and 975 cm^{-1}; NMR ($CDCl_3$) δ 3.00 (s, 3 H), 3.62 (s, 3 H), 4.87 (d, 1 H, J = 12.7 Hz), 4.97 (s, 1 H), 5.15 (d, 1 H, J = 12.7 Hz), 7.28–7.37 (m, 5 H), 7.44–7.72 (m, 2 H), 7.88 (d, 1 H, J = 8.2 Hz), and 8.32 (dd, 1 H, J = 8.3 and 0.8 Hz).

This material was subjected to sulfenate ester cleavage using the trimethyl phosphite procedure to give 4-carbomethoxy-5-(hydroxymethyl)-2-methyl-3-phenyl-Δ^4-isoxazoline (**39**) as a colorless oil in 69% yield: IR (neat) 3420, 3030, 2970, 1720–1640, 1440, 1365, 1230, 1130, 1100, 1040, 750, and 705 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.94 (s, 3 H), 3.64 (s, 3 H), 4.52 (s, 1 H), 4.90 (s, 1 H), and 7.28–7.37 (m, 5 H); HRMS calcd for $C_{13}H_{15}NO_4$ 249.1001, found 249.1002.

Reaction of Methyl 2-[(2-Nitrophenyl)sulfinyl]-2,3-butadienoate (6d) with *N*-*tert*-Butyl-*C*-phenylnitrone. A 180-mg sample of *N*-*tert*-butyl-*C*-phenylnitrone and 250 mg of allene **6d** in 5 mL of methylene chloride was stirred at 0 °C under a nitrogen atmosphere for 30 min. Removal of the solvent under reduced pressure left a crude yellow oil that was subjected to flash chromatography on a silica gel column using a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 2-*tert*-butyl-4-carbomethoxy-5-[[(2,4-dinitrophenyl)sulfenyloxy]methyl]-3-phenyl-Δ^4-isoxazoline (**40**), which was isolated as a yellow oil in 90% yield: IR (neat) 3040, 2995, 2885, 1715, 1510, 1330, 1315, 1240, 1100, 890, and 750 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.10 (s, 9 H), 3.45 (s, 3 H), 4.67 (d, 1 H, J = 12.6 Hz), 5.06 (d, 1 H, J = 12.6 Hz), 5.27 (s, 1 H), 7.12–7.27 (m, 6 H), 7.59–7.65 (m, 1 H), 7.78 (dd, 1 H, J = 8.3 and 1.2 Hz), and 8.19 (dd, 1 H, J = 8.3 and 1.2 Hz).

This material was subjected to sulfenate ester cleavage using the trimethyl phosphite procedure to give 2-*tert*-butyl-4-carbomethoxy-5-(hydroxymethyl)-3-phenyl-Δ^4-isoxazoline (**41**) as a pale yellow oil in 74% yield: IR (neat) 3450, 2985, 1690, 1640, 1365, 1240, 1205, 1090, 910, and 730 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.03 (s, 9 H), 3.55 (s, 3 H), 4.40 (s, 3 H), 5.22 (s, 1 H), and 7.23–7.30 (m, 5 H); HRMS calcd for $C_{16}H_{21}NO_4$ 291.1470, found 291.1468.

Cycloaddition of Benzonitrile Oxide with [(2,4-Dinitrophenyl)sulfinyl]-1,2-propadiene (6c). To a stirred solution containing 500 mg of benzohydroxamyl chloride[59] in 40 mL of carbon tetrachloride was added 325 mg of triethylamine at 0 °C. After the solution was stirred for several min, 813 mg of allene **6c** was added, and the resulting mixture was stirred at 0 °C for 2 h and then at room temperature for 1 h. The solution was filtered and dried over magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography using a 20% ethyl acetate–hexane mixture to give 720 mg (80%) of 5-[[(2,4-dinitrophenyl)-sulfenyloxy]methyl]-3-phenylisoxazole (**42**) as a yellow solid: mp 144–145 °C; IR (KBr) 3100, 1600, 1500, 1440, 1340, 1300, 1140, 1090, 960, and 920 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 5.14 (s, 2 H), 6.73 (s, 1 H), 7.52 (m, 3 H), 7.83 (m, 2 H), 8.06 (d, 1 H, J = 9 Hz), 8.52 (dd, 1 H, J = 9 and 2 Hz), and 9.13 (d, 1 H, J = 2 Hz). Anal. Calcd for $C_{16}H_{11}N_3O_6S$: C, 51.47; H, 2.95; N, 11.26; S, 8.58. Found: C, 51.53; H, 2.98; N, 11.23; S, 8.51.

To a stirred solution containing 500 mg of 5-[[(2,4-dinitrophenyl)sulfenyloxy]methyl]-3-phenylisoxazole (**42**) in 50 mL of tetrahydrofuran at −78 °C under a nitrogen atmosphere was added 0.92 mL of a 1.6 M *n*-butyllithium solution in hexane. The solution was stirred at −78 °C for 10 min and then allowed to warm to room temperature. The reaction mixture was poured onto a saturated ammonium chloride solution and extracted with ether. The combined ether extracts were washed with water and brine and dried over anhydrous sodium sulfate to afford a yellow residue. This residue was purified to give 5-(hydroxymethyl)-3-phenylisoxazole (**43**) as a colorless oil: IR (neat) 3400, 1600, 1320, 1440, 1410, 1350, and 910 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.82 (s, 2 H), 6.61 (s, 1 H), 7.41 (m, 3 H), and 7.85 (m, 2 H). Anal. Calcd for $C_{10}H_9NO_2$: C, 68.55; H, 5.18; N, 7.01. Found: C, 68.52; H, 5.07; N, 6.85.

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Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra (75 MHz) for all compounds with high-resolution mass spectra (7 pages). Ordering information is given on any current masthead page.

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