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# Access to Ring-Fused Homo- and Heteroaromatic Derivatives via an Initial Ring-Opening of 3-Nitro-4-(phenylsulfonyl)thiophene[1]

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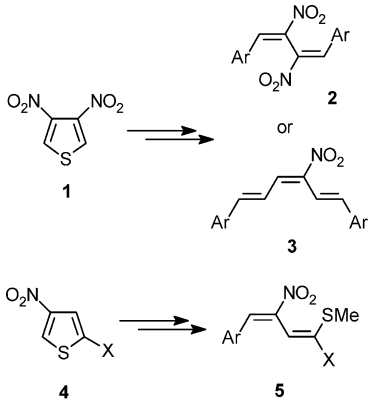
*Received February 28, 2003*

Within an overall ring-opening/ring-forming protocol, the (*E*,*E*)-4-methylthio-2-nitro-3-phenylsulfonyl-1-pyrrolidino-1,3-butadiene (**7**) [derived from the initial opening of 3-nitro-4-(phenylsulfonyl)-thiophene (**6**) with pyrrolidine and silver nitrate in EtOH] is revealed to be an excellent precursor of nitro(phenylsulfonyl) derivatives of ring-fused aromatic (naphthalene, phenanthrene) or heteroaromatic (benzothiophene) compounds whose substitution pattern cannot be easily achieved by conventional methods. The key step is represented by a thermal electrocyclic rearrangement of (*E*,*E*)-1-aryl-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadienes (**9**), which, thanks to proper geometric and electronic factors, occurs in unprecedentedly mild conditions and is followed by an irreversible, concerted syn $\beta$-elimination of methanesulfinic acid to aromatize the newly formed cyclohexadienic ring.

## Introduction

Within the framework of the well-recognized nonbenzenoid behavior of the thiophene heterocycle,[2−4] the initial, amine-induced, ring-opening of nitrothiophenes **1**[2a,c,3] and **4**[2b,4] has been shown to provide access to interesting polyfunctionalized molecules such as dinitrobutadienes **2** or nitrohexatrienes **3**, and nitrobutadienes **5**, respectively (Chart 1), which represent powerful building blocks amenable to further manipulation. In particular, an overall ring-opening/ring-closure procedure has recently allowed the attainment of benzene derivatives,[3a] as well as heteroaromatic compounds such as isoxazoles,[2a,b,5] furoxans,[6] furazans,[6] or pyrroles.[3b]

**CHART 1**




As a novel, significant example of the applicability of such a procedure to the construction of a homoaromatic ring starting from a 3-nitrothiophene, herein we report on an effective transformation of 3-nitro-4-(phenylsulfonyl)thiophene (**6**) into ring-fused aromatic derivatives functionalized with vicinal nitro and phenylsulfonyl groups (**10**).

## Results and Discussion

The overall ring-to-ring transformation described in the present paper is summarized in Scheme 1. The effective preparation of compounds **10** takes advantage of a final, surprisingly simple, benzene-ring forming cyclization (step e) following ring-opening of 3-nitro-4-(phenylsulfonyl)thiophene (**6**) (steps a and b), replacement of the

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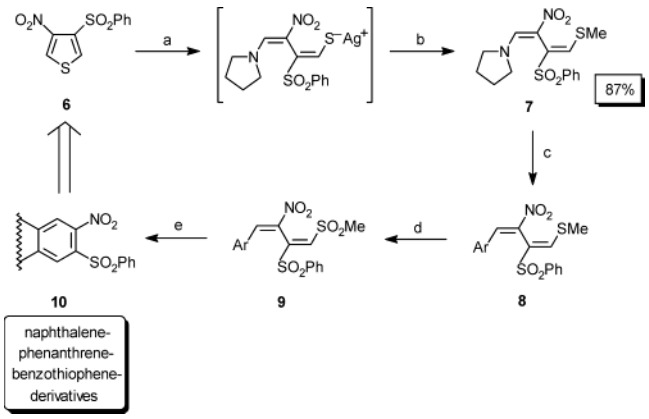
10.1021/jo034264q CCC: $25.00 
Published on Web 05/31/2003

**SCHEME 1**[a]




[a] Reagents and conditions: (a) **6** (1.1 mmol), pyrrolidine (2 mol equiv), $AgNO_3$ (2 mol equiv), in absolute ethanol (10 mL), 40 °C, 15 h; (b) MeI (10 mmol), rt, 4 h; (c) [**7**]: ca. 0.08 M in THF; ArMgBr: 1.1 mol equiv; 0 °C; then, $H_3O^+$ quenching; (d) [**8**]: 0.07 M in $CH_2Cl_2$; *m*-chloroperbenzoic acid: 2 mol equiv; rt; (e) [**9**]: $5 \times 10^{-3}$ M in dry *p*-xylene; reflux, 1−70 h.

**TABLE 1. Yields of Compounds 8 and 9 from Steps c and d of Scheme 1**[a]

| Ar | **8**: %[a] | **9**: %[a] |
|---|---|---|
| Ph | **8a**: 90 | **9a**: 95 |
| 2-$MeC_6H_4$ | **8b**: 98 | **9b**: 98 |
| 3-$MeC_6H_4$ | **8c**: 95 | **9c**: 98 |
| 4-$MeC_6H_4$ | **8d**: 90 | **9d**: 92 |
| 4-$MeOC_6H_4$ | **8e**: 89 | **9e**: 98 |
| 4-(COOMe)$C_6H_4$ | **8f**: 67 | **9f**: 81 |
| 1-naphthyl | **8g**: 98 | **9g**: 99 |
| 2-naphthyl | **8h**: 98 | **9h**: 99 |
| 2-thienyl | **8i**: 98 | **9i**: 99 |
| 3-thienyl | **8j**: 77 | **9j**: 98 |

[a] Yields of isolated products.

**TABLE 2. Yields of Ring-Fused Compounds 10 from the Oxidative Cyclization of 9 in Dry *p*-Xylene**[a]

| Ar | product | yield (%)[b] | reaction time (h)[c] |
|---|---|---|---|
| Ph | **10a** | 96 | 48 |
| 2-$MeC_6H_4$ | **10b** | 98 | 24 |
| 3-$MeC_6H_4$ | **10c**/**10c′**[d] | 93 | 17 |
| 4-$MeC_6H_4$ | **10d** | 90 | 70 |
| 4-$MeOC_6H_4$ | **10e** | 81 | 24 |
| 4-(COOMe)$C_6H_4$ | **10f** | 67 | 28 |
| 1-naphthyl | **10g** | 88 | 1.5 |
| 2-naphthyl | **10h** | 98 | 1.0 |
| 2-thienyl | **10i** | 90 | 20 |
| 3-thienyl | **10j** | 98 | 16 |

[a] [**9**]: $5 \times 10^{-3}$ M in dry *p*-xylene; reflux (1−70 h). [b] Isolated yields. [c] Reaction followed by TLC disappearance of substrate. [d] Mixture of isomeric **10c** and **10c′** from which the single components could not be separated in pure form: **10c**/**10c′** ratio = 66/34 ($^1$H NMR analysis).

pyrrolidino moiety of **7** (step c), and oxidation of the methylthio group of **8** (step d). Yields of compounds **8** and **9** are collected in Table 1; cyclization yields are collected in Table 2.

In particular, it should be noted that the ring-opening of **6** effectively occurs in the presence of silver ions, leading (after methylation of the envisageable, although nonisolated, intermediate silver thiolate) to the appealingly functionalized butadiene **7**, an outcome undoubtedly much akin to that reported for the 2-X-4-nitrothiophenes **4**.[2b,4] The assignment of the (*E*,*E*)-configuration to **7** is founded on an X-ray single-crystal structure determination.[7]

It is interesting to note that the amine attack on **6** is chemoselectively directed toward the C(2) atom, while reactions with arenethiolates on the same substrate have been reported[8] to lead to a mixture of *cine*-substitution products resulting from attack of the nucleophile to C(2) (main pathway) or C(5).

The replacement of the pyrrolidino group of **7** with an aryl moiety has been accomplished by means of a procedure already applied with success to butadienes derived from ring-opening of **1**[2b] and **4**.[9,10] In tight analogy with the latter cases, only the nitroenamine system undergoes attack by the Grignard reagent, the yields of the resulting aryl derivatives **8** being excellent throughout (Table 1).

The stereochemical assignment to compounds **8** essentially rests on an NMR analysis on the model compound **8i** (Ar = 2-Th). Thus, NOE experiments showed that irradiation of H(4) caused a 2.64% NOE enhancement for the H(2′) and H(6′) protons of the phenylsulfonyl group, besides a 6.62% enhancement for the SMe protons; on the other hand, irradiation of SMe caused no appreciable NOE effect for the H(2′) and H(6′) protons, besides a 3.53% enhancement for H(4). On this basis, an (*E*)-configuration can be assigned to the C(3)−C(4) vinylic system of **8**. With regard to the C(1)−C(2) vinylic system, a likewise (*E*)-configuration is supported by the marked deshielding experienced by the proton adjacent to the nitro group, relevant $\delta$ values being higher than 8.2 ppm throughout.[4] It should also be remarked that, in those cases where the C(3) multiplet could be observed [such as **8d** (Ar = *p*-Tol) or **8i** (Ar = 2-Th)] the $^3J_{C3-H1}$ values found (8.0 and 6.8 Hz, respectively) compare well with trans $^3J_{CH}$ values (ranging from 8.2 to 11.8 Hz) previously reported for diene−$Fe(CO)_3$ complexes:[11] cis $^3J_{CH}$ values ranging from 3.4 to 4.6 Hz.[11] Such results in particular confirm that, also in the present case, the replacement of the amino moiety in the nitroenamine portion with the aryl of the Grignard reagents occurs with retention of configuration, as already observed in other similar cases.[4,9,10a]

**Thermal Cyclization of Compounds 9.** The key step of the overall **6** to **10** sequence of Scheme 1 is undoubtedly represented by the cyclization (step e), whereby a nitro(phenylsulfonyl)-substituted benzene ring is obtained through annulation accompanied by methanesulfinic acid elimination (Scheme 2).

As a matter of fact, as a first attempt to exploit the high degree of functionalization of compounds **9**, recent reports on the behavior of *trans*-1,2-bis(arylsulfonyl)-

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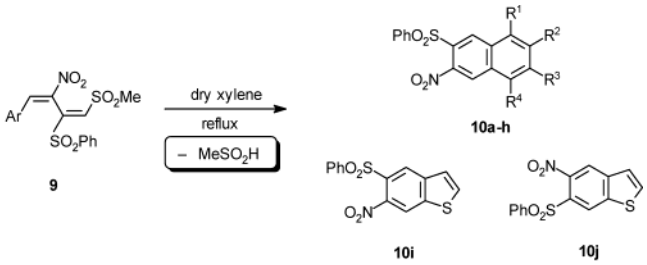
**SCHEME 2**




**10a**: $R^1 = R^2 = R^3 = R^4 = H$
**10b**: $R^1 = R^2 = R^3 = H$; $R^4 = Me$
**10c**: $R^1 = R^2 = R^4 = H$; $R^3 = Me$
**10c'**: $R^2 = R^3 = R^4 = H$; $R^1 = Me$
**10d**: $R^1 = R^3 = R^4 = H$; $R^2 = Me$
**10e**: $R^1 = R^3 = R^4 = H$; $R^2 = MeO$
**10f**: $R^1 = R^3 = R^4 = H$; $R^2 = COOMe$
**10g**: $R^1 = R^2 = H$; $R^3,R^4$ =
**10h**: $R^3 = R^4 = H$; $R^1,R^2$ =

ethylenes as valuable dienophiles[12] suggested the employment of **9** in Diels–Alder processes. Surprisingly enough, from the model reaction of **9d** with 1,3-cyclohexadiene in refluxing toluene for 1 day, the workup led to the isolation, besides some recovered substrate, of a main product that was identified as 6-methyl-2-nitro-3-(phenylsulfonyl)naphthalene (**10d**). The formation of **10d** was found to be independent of the presence of cyclohexadiene, efficiently occurring when heating **9d** alone at reflux in the same solvent.

The synthetic interest of such an outcome prompted us to extend the process to the whole series of **9** in our hands after optimization of the experimental conditions, eventually selecting the higher boiling *p*-xylene for the initially employed toluene. The results of Table 2 clearly show that operatively simple, relatively mild reaction conditions meet with results which are excellent throughout; it should be noticed that the prompt reactivity of the naphthyl derivatives **9g**,**h** (reaction complete within 1.5 and 1 h, respectively) indicates they are particularly suitable systems.

As expected, with the phenyl- (**9a**) and the 4-substituted phenyl derivatives (**9d**–**f**) cyclization concerns at one of the two (equivalent) positions ortho to the butadiene system, while the 2-methyl group of **9b** directs the cyclization onto the free 6-position; interestingly, with the 3-tolyl derivative **9c** it was possible to isolate a mixture of the two nonseparable isomeric products corresponding to cyclization at the 6-position (**10c**) or at the 2-position (**10c′**) of the aromatic ring, some regioselectivity showing up in the sizable preference (**10c**/**10c′** = 66/34) for the less hindered 6-position.

Of particular relevance is the possibility of obtaining, in similar excellent yields, isomeric nitro(phenylsulfonyl) phenanthrenes (**10g**,**h**) and benzothiophenes (**10i**,**j**) simply by means of an appropriate choice of the Grignard reagent for step c of Scheme 1. Interestingly enough, the formation of **10h** from **9h** as the sole product is the result of a complete regioselectivity, annulation exclusively occurring at the naphthalene α-position adjacent to the butadiene chain.

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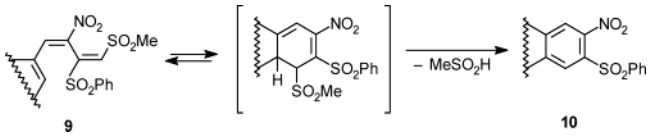
**SCHEME 3**




From a practical point of view, it should be stressed that the protocol herein allows the access to, e.g., polysubstituted naphthalenes or phenanthrenes which are difficult, if not impossible, to prepare through conventional synthetic methodologies, such as those based on electrophilic aromatic substitutions. As a matter of fact the general approach hinging on the cycloaddition (inter- or intramolecular) of suitable precursors is frequently exploited, e.g., for the synthesis of properly substituted naphthalene moieties, whose interest in the biological and/or pharmaceutical fields is, on the other hand, well-known.[13]

From a mechanistic point of view, for the present cyclization we can envisage an initial electrocyclic rearrangement, eventually followed by an irreversible methanesulfinic acid elimination (Scheme 3).[14]

Within this framework, an aspect that is surely intriguing is represented by the unprecedented mildness of the experimental conditions (reflux in *p*-xylene) necessary to perform the cyclization on compounds **9**. As a matter of fact, e.g., the benzocyclization of 1-aryl-1,3-butadienes has been reported[13b,15] until recently to occur in much harsher thermal conditions such as flash vacuum pyrolysis,[15a] or with acid catalysis[13b] or photostimulation.[15b] Further examples of the participation of two $\pi$-electrons of an aromatic ring in an electrocyclization process are essentially confined to the photochemical conversions, under oxidizing conditions, of stilbenes[16a] or heterostilbenes[16b] to phenanthrenes or heterophenanthrenes, respectively, or of styrylanthracenes to more complex fused systems.[16c]

Most likely a number of factors concur to the facility of the overall process herein, namely (a) a proper configuration, hence a proper spatial arrangement of the molecule, which brings to the correct distance the two carbon atoms involved in the formation of the new bond, (b) favorable electronic effects of the substituents on the

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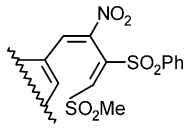
butadiene chain, and (c) the possibility of an irreversible aromatization due to a favorable $\beta$-elimination of methanesulfinic acid, which prevents the possibility of isolating any reaction intermediate.

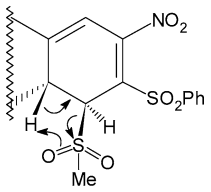
As far as the former factor above is concerned, the (*E*,*E*)-configuration of compounds **9** allows the molecule to attain the s-cis conformation (**A**) required for intramolecular cyclization.




**A**

With regard to the substituent effects in the butadiene moiety, it should be stressed that no significant reaction has been observed on the sulfide **8d** either in the same experimental conditions used for **9d** or in the presence of DDQ, which should be able to perform dehydrogenation of the newly formed ring: thus, the presence of the methylsulfonyl group at C(4) seems essential[17] not simply to accomplish rearomatization (providing a good leaving group for the final elimination step), but also for the cycloaddition step itself.

Finally, thanks to the disrotatory nature of the thermal electrocyclization process herein, the starting (*E*)-configuration of the C(3)−C(4) double bond most likely leads to a cyclohexadiene intermediate (see Scheme 3) where the $SO_2Me$ group and the adjacent ring hydrogen are cis: such a relative position justifies, in the neutral reaction conditions employed, an easy, concerted syn $\beta$-elimination as schematized in **B**.




**B**

## Conclusions

The results reported herein depict a useful, high-yielding, overall ring−ring interconversion whereby 3-nitro-4-(phenylsulfonyl)thiophene (**6**) is transformed, in generally good overall yields, into appealing ring-fused aromatic or heteroaromatic derivatives whose substitution pattern cannot be easily achieved via conventional methodologies. The most interesting aspects of the overall sequence are represented by the initial transformation of **6** into the (*E*,*E*)-1-aryl-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadienes **8** and by the thermal electrocyclization step whose unprecedentedly mild conditions are surely due to the concurrence of particularly favorable geometric and electronic factors. The final, irreversible elimination of methanesulfinic acid on the nonisolable cyclohexadienic intermediate takes in turn advantage of its stereochemistry, which allows a concerted syn $\beta$-elimination.

## Experimental Section

**General.** Unless differently specified, $^1$H NMR and $^{13}$C NMR spectra were recorded at 200 and 50 MHz, respectively; chemical shifts (TMS as internal reference) are reported as $\delta$ ppm. Melting points are uncorrected. Silica gel 230−400 mesh was used for column chromatography, all solvents being distilled before use. Tetrahydrofuran (THF) was purified by standard methods and distilled over potassium benzophenone ketyl before use. 3-Nitro-4-(phenylsulfonyl)thiophene (**6**) was synthesized as previously reported[18a] from methyl 3-bromo-2-thiophenecarboxylate, which was in turn obtained by the action of diazomethane on the corresponding acid.[18b] Commercial 2- and 3-bromothiophene as well as 1- and 2-bromonaphthalene were used as received after drying over molecular sieves (4 Å) or (for the latter) over P2O5 under vacuum; methyl 4-iodobenzoate was prepared from the corresponding commercial acid by reaction with diazomethane in ether. All other commercially available reagents were used as received.

**Ring-Opening of 3-Nitro-4-(phenylsulfonyl)thiophene (6).** A suspension of 3-nitro-4-(phenylsulfonyl)thiophene (0.3 g, 1.1 mmol) in absolute ethanol (10 mL), under argon and magnetic stirring, was heated to 40 °C and 0.38 g (2.2 mmol) of silver nitrate was added; after 15 min pyrrolidine (0.18 mL, 2.2 mmol) was introduced and the reaction mixture was kept overnight at 40 °C under magnetic stirring. The reaction mixture was cooled to room temperature and MeI (0.62 mL, 10 mmol) was added; after 4 h under magnetic stirring, the reaction was diluted with acetone and filtered from a gray precipitate, which was washed with acetone. The clear filtrate was evaporated under reduced pressure to leave a residue that was dissolved in dichloromethane and chromatographed on a silica gel column (eluants: dichloromethane and then a gradient of the latter with ethyl acetate). Unreacted thiophene derivative (**10**) was eluted first (18 mg, 6%), followed by the product (**7**) (0.34 g, 87%).

**4-Methylthio-2-nitro-3-phenylsulfonyl-1-pyrrolidino-1,3-butadiene (7).** Yellowish solid, mp 190.6−191.2 °C (EtOH); $\nu_{max}$ (Nujol) 1611, 1572, 1403, 1295, 1265, 1238, 1140, 1086 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.99 (4H, m), 2.52 (3H, s), 3.32 (1H, m), 3.72 (2H, m), 4.05 (1H, m), 7.51 (3H, m), 7.83 (2H, m), 8.13 (1H, s), 8.66 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 17.35, 24.45, 26.04, 47.56, 55.79, 112.32, 127.04, 128.30, 128.96, 133.41, 140.09, 148.48, 155.03. Anal. Calcd for $C_{15}H_{18}N_2O_4S_2$: C, 50.8; H, 5.1; N, 7.9. Found: C, 50.7; H, 5.2; N, 8.0.

**Arylmagnesium Halides**. All the Grignard reagents were THF or $Et_2O$ solutions titrated[19] just before use. Commercial solutions in THF or $Et_2O$ of phenyl-, of 2-, 3-, and 4-methylphenyl-, and of 4-methoxyphenylmagnesium bromides or chlorides were used as received. 1-Naphthyl-, 2-naphthyl-, and 2-thienylmagnesium bromides were prepared in THF by standard methods. 3-Thienylmagnesium bromide in THF was synthesized by the entrainment method with 1,2-dibromoethane[20] in analogy with a reported procedure.[21] Following a literature procedure,[22] the 4-methoxycarbonyl phenylmagnesium halide was obtained in THF by exchange reaction with freshly prepared isopropylmagnesium bromide of the corresponding methyl iodobenzoate.

(17) Preliminary results suggest that the phenylsulfonyl goup at C(3) is, on the contrary, not essential for the cyclization process to occur.

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**Reactions of 7 with Aryl Grignard Reagents.** To a suspension of 4-methylthio-2-nitro-3-phenylsulfonyl-1-pyrrolidino-1,3-butadiene (**7**; 0.354 g, 1 mmol) in THF (12 mL), cooled to 0 °C, was slowly added by syringe the Grignard reagent in THF (1.1 mmol) under argon and magnetic stirring. The reaction mixture was left to reach room temperature, kept under stirring for 15 min (the end of the reaction being judged by TLC analysis), and eventually poured into a dichloromethane-ice−HCl (1.1 mmol) mixture. After separation of the two layers, the aqueous phase was extracted with dichloromethane; the collected organic extracts were washed with water and dried over $Na_2SO_4$. Concentration under vacuum of the extracts gave a crude that was purified by column chromatography over silica gel (petroleum ether/dichloromethane gradients as eluent). Yields of compounds **8** are collected in Table 1.

***(E,E)*-4-Methylthio-2-nitro-1-phenyl-3-phenylsulfonyl-1,3-butadiene (8a).** Yellow solid, mp 101.2−102.4 °C (EtOH); $\nu_{max}$ (Nujol) 1643, 1552, 1521, 1446, 1310, 1208, 1150, 1086 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.53 (3H, s), 7.43 (8H, m), 7.77 (2H, m), 8.27 (1H, s), 8.30 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.66, 125.72, 128.21, 128.99, 129.08, 129.70, 130.84, 132.13, 133.64, 139.17, 139.50, 141.15, 155.86. Anal. Calcd for $C_{17}H_{15}NO_4S_2$: C, 56.5; H, 4.2; N, 3.9. Found: C, 56.7; H, 4.3; N, 4.0.

***(E,E)*-1-(2-Methylphenyl)-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (8b).** Yellowish solid, mp 140.2−141.8 °C (EtOH); $\nu_{max}$ (Nujol) 1641, 1559, 1522, 1316, 1306, 1226, 1152, 1086 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.35 (3H, s), 2.53 (3H, s), 7.10 (2H, m), 7.38 (5H, m), 7.72 (2H, m), 8.20 (1H, s), 8.50 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.74, 20.11, 125.57, 126.35, 127.96, 128.06, 128.96, 129.32, 130.54, 131.52, 133.45, 138.95, 139.37, 139.51, 140.06, 156.14. Anal. Calcd for $C_{18}H_{17}NO_4S_2$: C, 57.6; H, 4.6; N, 3.7. Found: C, 57.8; H, 4.7; N, 3.9.

***(E,E)*-1-(3-Methylphenyl)-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (8c)**. Yellow solid, mp 108.3−109.4 °C (EtOH); $\nu_{max}$ (Nujol) 1645, 1559, 1519, 1318, 1306, 1293, 1166, 1150, 1087 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.30 (3H, s), 2.53 (3H, s), 7.21 (3H, m), 7.41 (4H, m), 7.77 (2H, m), 8.26 (2H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.62, 21.30, 125.89, 127.60, 128.18, 128.89, 129.03, 129.60, 131.82, 133.04, 133.53, 138.59, 138.95, 139.59, 141.28, 155.73. Anal. Calcd for $C_{18}H_{17}NO_4S_2$: C, 57.6; H, 4.6; N, 3.7. Found: C, 57.8; H, 4.7; N, 3.9.

***(E,E)*-1-(4-Methylphenyl)-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (8d).** Yellow solid, mp 107.9−108.9 °C (EtOH); $\nu_{max}$ (Nujol) 1640, 1605, 1524, 1446, 1313, 1213, 1186, 1146, 1084 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.37 (3H, s), 2.52 (3H, s), 7.14 (2H, half AA′BB′, $J$ = 8.1 Hz), 7.46 (5H, m), 7.78 (2H, m), 8.26 (1H, s), 8.29 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.59, 21.66, 126.40, 127.09, 128.30, 129.06, 129.84, 131.13, 133.49, 138.39, 139.85, 141.21, 143.22, 155.39. Anal. Calcd for $C_{18}H_{17}NO_4S_2$: C, 57.6; H, 4.6; N, 3.7. Found: C, 57.6; H, 4.7; N, 3.7.

***(E,E)*-1-(4-Methoxyphenyl)-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (8e).** Yellow solid, mp 136.0−137.2 °C (EtOH); $\nu_{max}$ (Nujol) 1643, 1600, 1551, 1525, 1322, 1309, 1268, 1179, 1147, 1087 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.52 (3H, s), 3.85 (3H, s), 6.87 (2H, half AA′BB′, $J$ = 8.8 Hz), 7.44 (3H, m), 7.56 (2H, half AA′BB′, $J$ = 8.8 Hz), 7.80 (2H, m), 8.27 (1H, s), 8.30 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.58, 55.51, 114.65, 122.15, 126.03, 128.23, 129.08, 133.52, 133.61, 136.34, 139.60, 141.22, 155.42, 163.08. Anal. Calcd for $C_{18}H_{17}NO_5S_2$: C, 55.2; H, 4.4; N, 3.6. Found: C, 55.4; H, 4.6; N, 3.6.

***(E,E)*-1-[4-(Methoxycarbonyl)phenyl]-4-methylthio-2-nitro-3-phenylsulfonyl-1,3-butadiene (8f)**. Yellow solid, mp 162.0−163.0 °C (EtOH); $\nu_{max}$ (Nujol) 1713, 1649, 1551, 1530, 1377, 1310, 1284, 1217, 1194, 1184, 1150, 1115, 1088 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.54 (3H, s), 3.94 (3H, s), 7.41 (3H, m), 7.53 (2H, half AA′BB′, $J$ = 8.6 Hz), 7.76 (2H, m), 7.96 (2H, half AA′BB′, $J$ = 8.6 Hz), 8.29 (2H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.76, 52.47, 125.21, 128.18, 129.18, 129.96, 130.30, 132.62, 133.74, 133.93, 139.29, 139.59, 141.02, 156.38, 166.03. Anal. Calcd for $C_{19}H_{17}NO_6S_2$: C, 54.4; H, 4.1; N, 3.3. Found: C, 54.4; H, 4.2; N, 3.4.

***(E,E)*-4-Methylthio-1-(1-naphthyl)-2-nitro-3-phenylsulfonyl-1,3-butadiene (8g)**. Yellow solid, mp 222.1−223.1 °C (toluene); $\nu_{max}$ (Nujol) 1642, 1521, 1446, 1307, 1243, 1141, 1082 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.56 (3H, s), 7.07 (3H, m), 7.33 (1H, app. t, $J$ = 7.7 Hz), 7.59 (5H, m), 7.85 (3H, m), 8.28 (1H, s), 9.02 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.82, 123.46, 125.27, 125.50, 126.58, 126.78, 127.23, 127.34, 127.89, 128.58, 128.83, 131.49, 132.04, 132.69, 133.31, 138.91, 141.13, 156.62. Anal. Calcd for $C_{21}H_{17}NO_4S_2$: C, 61.3; H, 4.2; N, 3.4. Found: C, 61.4; H, 4.3; N, 3.3.

***(E,E)*-4-Methylthio-1-(2-naphthyl)-2-nitro-3-phenylsulfonyl-1,3-butadiene (8h)**. Yellow solid, mp 131.4−132.4 °C (EtOH); $\nu_{max}$ (Nujol) 1643, 1621, 1598, 1548, 1519, 1446, 1344, 1309, 1177, 1144, 1084 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.53 (3H, m), 7.35 (3H, m), 7.56 (3H, m), 7.78 (5H, m), 7.99 (1H, br s), 8.32 (1H, s), 8.48 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.67, 125.12, 125.99, 126.90, 127.38, 127.72, 128.21, 128.58, 128.87, 129.05, 129.10, 132.85, 133.53, 133.87, 134.84, 139.09, 139.55, 141.35, 155.93. Anal. Calcd for $C_{21}H_{17}NO_4S_2$: C, 61.3; H, 4.2; N, 3.4. Found: C, 61.5; H, 4.2; N, 3.3.

***(E,E)*-4-Methyltio-2-nitro-3-phenylsulfonyl-1-(2-thienyl)-1,3-butadiene (8i)**. Yellow solid, mp 62.5−63.5 °C (EtOH); $\nu_{max}$ (Nujol) 1629, 1546, 1508, 1414, 1304, 1217, 1145, 1084, 1055 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.54 (3H, s), 7.12 (1H, dd, $J$ = 3.8 and 4.9 Hz), 7.50 (4H, m), 7.65 (1H, d, $J$ = 4.9 Hz), 7.82 (2H, m), 8.34 (1H, s), 8.53 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.60, 125.31, 127.99, 128.19, 129.42, 132.94, 133.63, 134.69, 135.36, 135.96, 137.82, 139.98, 157.43. Anal. Calcd for $C_{15}H_{13}NO_4S_3$: C, 49.0; H, 3.6; N, 3.8. Found: C, 49.0; H, 3.7; N, 3.7.

***(E,E)*-4-Methyltio-2-nitro-3-phenylsulfonyl-1-(3-thienyl)-1,3-butadiene (8j).** Yellow solid, mp 59.0−60.0 °C (EtOH); $\nu_{max}$ (Nujol) 1635, 1549, 1516, 1308, 1252, 1146, 1086 $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) $\delta$ 2.66 (3H, s), 7.13 (1H, dd, $J$ = 1.2 and 5.2 Hz), 7.38 (1H, dd, $J$ = 3.2 and 5.2 Hz), 7.55 (3H, m), 7.80 (2H, m), 8.03 (1H, dd, $J$ = 1.2 and 3.2 Hz), 8.39 (1H, s), 8.49 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.60, 126.00, 127.24, 127.42, 128.21, 129.12, 131.77, 133.70, 134.69, 134.81, 137.52, 139.56, 155.54. Anal. Calcd for $C_{15}H_{13}NO_4S_3$: C, 49.0; H, 3.6; N, 3.8. Found: C, 49.2; H, 3.8; N, 3.8.

**Oxidation of Sulfides 8 to Sulfones 9.** To a solution of the methyl sulfide **8** (0.5 mmol) in dichloromethane (7.5 mL), kept at room temperature and under magnetic stirring, was added 0.26 g of 66% *m*-chloroperbenzoic acid (1 mmol). The end of the reaction was judged both by disappearance of the substrate (TLC) and by a negative KI spot-test for the peracid. The mixture was diluted with dichloromethane, washed with 5% aqueous $Na_2SO_3$ and $NaHCO_3$ solutions, and eventually dried over $Na_2SO_4$. After filtration and removal of the solvent under reduced pressure a crude residue was obtained, generally pure by $^1H$ NMR analysis. Yields of the methylsulfonyl derivatives **9** are reported in Table 1.

***(E,E)*-4-Methylsulfonyl-2-nitro-1-phenyl-3-phenylsulfonyl-1,3-butadiene (9a).** Yellowish solid, mp 190.4−190.9 °C (EtOH); $\nu_{max}$ (Nujol) 1649, 1594, 1572, 1522, 1326, 1308, 1243, 1214, 1187, 1161, 1148, 1086, 1040, 1001 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 3.01 (3H, s), 7.38 (7H, m), 7.56 (1H, m), 7.76 (2H, m), 7.94 (1H, s), 8.38 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 42.50, 129.20, 129.47, 129.55, 131.17, 132.49, 135.37, 136.13, 141.83, 141.88, 146.00; $^{13}C$ NMR ($CD_3COCD_3$) $\delta$ 42.73, 129.82, 130.22, 130.42, 130.52, 132.11, 133.02, 136.16, 137.29, 138.14, 141.62, 144.91, 145.05. Anal. Calcd for $C_{17}H_{15}NO_6S_2$: C, 51.9; H, 3.8; N, 3.6. Found: C, 52.0; H, 4.0; N, 3.6.

***(E,E)*-1-(2-Methylphenyl)-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (9b).** Yellow solid, mp 179.4−181.0 °C (EtOH); $\nu_{max}$ (Nujol) 1655, 1596, 1529, 1447, 1323, 1229, 1151, 1085, 1030 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.34 (3H, s), 2.98 (3H, s), 7.14 (2H, m), 7.27 (1H, d, $J$ = 7.4 Hz), 7.37 (3H, m), 7.54 (1H, m), 7.70 (2H, m), 7.87 (1H, s), 8.60 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.15, 42.30, 126.61, 128.59, 129.12, 129.41, 130.89, 131.96, 135.13, 136.16, 136.49, 139.58, 139.97, 142.08, 145.63; $^{13}C$ NMR ($CD_3COCD_3$) $\delta$ 20.10, 42.59, 127.04, 129.08, 129.87, 129.92, 130.47, 131.70, 132.48, 135.98, 137.96, 138.37,

139.87, 140.65, 144.58, 145.12. Anal. Calcd for $C_{18}H_{17}NO_6S_2$: C, 53.1; H, 4.2; N, 3.4. Found: C, 53.3; H, 4.4; N, 3.5.

**(*E*,*E*)-1-(3-Methylphenyl)-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (9c).** Yellow solid, mp 175.3−176.7 °C (EtOH); $\nu_{max}$ (Nujol) 1650, 1579, 1520, 1325, 1242, 1182, 1160, 1149, 1087, 1042 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.31 (3H, s), 3.02 (3H, s), 7.24 (4H, m), 7.39 (2H, m), 7.55 (1H, m), 7.75 (2H, m), 7.93 (1H, s), 8.35 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.24, 42.50, 128.03, 129.09, 129.45, 132.05, 133.38, 135.20, 135.35, 136.24, 138.90, 141.85, 141.99, 146.10; $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 21.14, 42.74, 129.36, 129.75, 130.18, 130.37, 130.47, 132.36, 133.83, 136.04, 137.26, 138.29, 139.49, 141.56, 144.92, 145.24. Anal. Calcd for $C_{18}H_{17}NO_6S_2$: C, 53.1; H, 4.2; N, 3.4. Found: C, 53.3; H, 4.4; N, 3.5.

**(*E*,*E*)-1-(4-Methylphenyl)-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (9d).** Whitish solid, mp 212.3-212.7 °C (toluene); $\nu_{max}$ (Nujol) 1657, 1605, 1523, 1334, 1317, 1311, 1191, 1165, 1154, 1144, 1087 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.37 (3H, s), 3.01 (3H, s), 7.15 (2H, half AA′BB′, $J$ = 8.3 Hz), 7.41 (4H, m), 7.58 (1H, m), 7.77 (2H, m), 7.93 (1H, s), 8.37 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.75, 42.52, 126.43, 129.48, 129.51, 130.03, 131.56, 134.43, 135.21, 136.34, 141.69, 142.15, 143.92, 146.39. Anal. Calcd for $C_{18}H_{17}NO_6S_2$: C, 53.1; H, 4.2; N, 3.4. Found: C, 53.1; H, 4.3; N, 3.5.

**(*E*,*E*)-1-(4-Methoxyphenyl)-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (9e).** Yellow solid, mp 200.2−201.4 °C (EtOH); $\nu_{max}$ (Nujol) 1656, 1593, 1510, 1332, 1318, 1301, 1272, 1176, 1154, 1140 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.01 (3H, s), 3,86 (3H, s), 6.87 (2H, half AA′BB′, $J$ = 9.2 Hz), 7.46 (4H, m), 7.59 (1H, m), 7.80 (2H, m), 7.92 (1H, s), 8.37 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.55, 55.60, 114.88, 121.67, 129.52, 132.63, 134.06, 135.28, 136.42, 141.55, 142.10, 146.70, 163.49. Anal. Calcd for $C_{18}H_{17}NO_7S_2$: C, 51.1; H, 4.1; N, 3.3. Found: C, 51.2; H, 4.2; N, 3.3.

**(*E*,*E*)-1-[4-(Methoxycarbonyl)phenyl]-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadiene (9f).** Yellow solid, mp 188.3−189.9 °C (EtOH); $\nu_{max}$ (Nujol) 1720, 1650, 1595, 1530, 1327, 1311, 1289, 1161, 1151, 1117, 1087, 1044, 1017 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.06 (3H, s), 3.94 (3H, s), 7.47 (5H, m), 7.74 (2H, m), 7.96 and 7.97 [3H, half AA′BB′ ($J$ = 8.4 Hz) and s partly overlapped], 8.39 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.55, 52.55, 129.45, 129.65, 130.11, 130.67, 132.91, 133.29, 135.46, 135.89, 137.33, 140.15, 142.28, 145.21, 165.81. Anal. Calcd for $C_{19}H_{17}NO_8S_2$: C, 50.5; H, 3.8; N, 3.1. Found: C, 50.8; H, 3.9; N, 3.2.

**(*E*,*E*)-4-Methylsulfonyl-1-(1-naphthyl)-2-nitro-3-phenylsulfonyl-1,3-butadiene (9g).** Yellow solid, mp 154.7−155.9 °C dec (EtOH); $\nu_{max}$ (Nujol) 1657, 1593, 1524, 1318, 1239, 1141, 1082 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.12 (3H, s), 6.94 (3H, m), 7.36 (1H, apparent t, $J$ = 7.7 Hz), 7.47 (2H, m), 7.57 (3H, m), 7.80 (3H, m), 8.01 (1H, s), 9.06 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.40, 123.67, 125.35, 126.53, 126.86, 127.46, 127.75, 128.73, 128.84, 128.90, 129.99, 131.39, 132.30, 133.34, 133.75, 135.46, 138.60, 142.85, 145.00. Anal. Calcd for $C_{21}H_{17}NO_6S_2$: C, 56.9; H, 3.9; N, 3.2. Found: C, 56.7; H, 3.8; N, 3.3.

**(*E*,*E*)-4-Methylsulfonyl-1-(2-naphthyl)-2-nitro-3-phenylsulfonyl-1,3-butadiene (9h).** Yellow solid, mp 188.9−190.0 °C (EtOH); $\nu_{max}$ (Nujol) 1647, 1625, 1591, 1515, 1325, 1307, 1273, 1239, 1190, 1158, 1146, 1085 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.04 (3H, s), 7.31 (3H, m), 7.44 (1H, dd, $J$ = 2.0 and 8.8 Hz), 7.57 (2H, m), 7.77 (5H, m), 7.95 (1H, br s), 8.01 (1H, s), 8.55 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.55, 125.21, 126.67, 127.19, 127.74, 128.96, 129.03, 129.14, 129.41, 132.74, 134.31, 134.78, 135.07, 136.16, 141.92, 142.10, 146.14; $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 42.86, 126.60, 127.89, 128.08, 128.55, 129.54, 129.61, 129.96, 130.19, 130.39, 133.72, 134.75, 135.61, 135.76, 137.39, 138.28, 141.65, 145.18, 145.25. Anal. Calcd for $C_{21}H_{17}NO_6S_2$: C, 56.9; H, 3.9; N, 3.2. Found: C, 57.0; H, 4.0; N, 3.4.

**(*E*,*E*)-4-Methylsulfonyl-2-nitro-3-phenylsulfonyl-1-(2-thienyl)-1,3-butadiene (9i).** Yellow solid, mp 193.2−193.6 °C dec (EtOH); $\nu_{max}$ (Nujol) 1643, 1592, 1518, 1413, 1327, 1314, 1292, 1257, 1217, 1158, 1147, 1086, 1053 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.05 (3H, s), 7.11 (1H, dd, $J$ = 4.0 and 5.0 Hz), 7.48 (3H, m), 7.63 (2H, m), 7.84 (2H, m), 7.96 (1H, s), 8.55 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.62, 128.52, 129.49, 129.58, 132.69, 135.20, 135.36, 135.64, 136.55, 138.37, 142.81, 146.08; $^{13}$C NMR ($CD_3COCD_3$) $\delta$ 42.67, 129.25, 130.22, 130.53, 133.85, 134.03, 135.52, 136.09, 136.74, 138.70, 139.70, 145.37, 145.68. Anal. Calcd for $C_{15}H_{13}NO_6S_3$: C, 45.1; H, 3.3; N, 3.5. Found: C, 45.2; H, 3.4; N, 3.5.

**(*E*,*E*)-4-Methylsulfonyl-2-nitro-3-phenylsulfonyl-1-(3-thienyl)-1,3-butadiene (9j)**. Yellow solid, mp 155.0−155.3 °C (EtOH); $\nu_{max}$ (Nujol) 1649, 1595, 1519, 1321, 1252, 1180, 1160, 1147, 1087, 1042 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.02 (3H, s), 7.17 (1H, dd, $J$ = 1.5 and 5.1 Hz), 7.30 (1H, dd, $J$ = 2.9 and 5.1 Hz), 7.46 (2H, m), 7.63 (1H, m), 7.81 (3H, m), 7.91 (1H, s), 8.38 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 42.62, 127.24, 127.77, 129.50, 129.54, 131.31, 133.78, 135.44, 135.50, 135.74, 136.19, 141.48, 146.28. Anal. Calcd for $C_{15}H_{13}NO_6S_3$: C, 45.1; H, 3.3; N, 3.5. Found: C, 45.3; H, 3.4; N, 3.7.

**Cyclization of Sulfones 9 to the Nitro(phenylsulfonyl) Derivatives 10.** 1-Aryl-4-methylsulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadienes **9** (0.1 mmol) were dissolved in dry *p*-xylene (20 mL) and the solution refluxed until TLC showed complete disappearance of the substrate (1−70 h). The solvent was evaporated under reduced pressure and the residue purified either by column chromatography or by crystallization. Yields of the nitro(phenylsulfonyl) derivatives **10** are reported in Table 2.

**3-Nitro-2-(phenylsulfonyl)naphthalene (10a).** White solid, mp 230.5−231.6 °C (toluene); $\nu_{max}$ (Nujol) 1535, 1349, 1319, 1152, 1134, 1120, 1086 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 7.59 (3H, s), 7.83 (2H, m), 8.03 (3H, m), 8.16 (1H, m), 8.38 (1H, s), 9.01 (1H, s); $^{13}$C NMR ($CDCl_3$) $\delta$ 126.16, 127.95, 128.94, 129.08, 129.80, 130.66, 131.20, 131.34, 133.07, 133.39, 133.71, 134.64, 141.10, 144.61. Anal. Calcd for $C_{16}H_{11}NO_4S$: C, 61.3; H, 3.5; N, 4.5. Found: C, 61.6; H, 3.7; N, 4.6.

**5-Methyl-3-nitro-2-(phenylsulfonyl)naphthalene (10b).** Yellow solid, mp 246.6−248.2 °C (toluene); $\nu_{max}$ (Nujol) 1536, 1353, 1308, 1149, 1130, 1069 cm$^{-1}$; $^1$H NMR ($CD_3SOCD_3$) $\delta$ 2.72 (3H, s), 7.75 (5H, m), 8.01 (2H, m), 8.28 (2H, d, $J$ = 7.4 Hz), 8.69 (1H,s), 9.17 (1H, s); $^{13}$C NMR ($CD_3SOCD_3$) $\delta$ 18.55, 122.74, 127.32, 128.19, 129.01, 129.36, 130.40, 131.83, 132.69, 132.91, 133.84, 135.00, 136.60, 140.66, 143.77. Anal. Calcd for $C_{17}H_{13}NO_4S$: C, 62.4; H, 4.0; N, 4.3. Found: C, 62.2; H, 4.3; N, 4.3.

**6-Methyl-3-nitro-2-(phenylsulfonyl)naphthalene (10c) and 1-Methyl-6-nitro-7-(phenylsulfonyl)naphthalene (10c′).** The isomers **10c** and **10c′** were obtained as a solid mixture (**10c**/**10c′** 66/34) from which the single components could not be separated in pure form. Assignments of $^1$H NMR signals were done on the basis of NOE and NOEDiff experiments. White solid mixture; $\nu_{max}$ (Nujol) 1535, 1351, 1313, 1155, 1125, 1087 cm$^{-1}$; $^1$H NMR (mixture, $CDCl_3$) $\delta$ 2.61 ($3H_{\mathbf{10c}}$, s), 2.88 ($3H_{\mathbf{10c'}}$, s), 7.63 ($4H_{\mathbf{10c}} + 5H_{\mathbf{10c'}}$, m), 7.79 ($1H_{\mathbf{10c}}$, s), 7.87 ($1H_{\mathbf{10c'}}$, d, $J$ = 7.8 Hz), 8.02 ($2H_{\mathbf{10c'}} + 3H_{\mathbf{10c}}$, m), 8.27 ($1H_{\mathbf{10c'}}$, s), 8.37 ($1H_{\mathbf{10c'}}$, s), 8.94 ($1H_{\mathbf{10c}}$, s), 9.14 ($1H_{\mathbf{10c'}}$, s); $^{13}$C NMR ($CDCl_3$), 11 quaternary carbon lines out of the 12 expected for the two isomers were resolved, $\delta$ 130.31, 130.78, 132.51, 134.04, 134.21, 137.22, 141.20, 141.30, 142.13, 144.40, 144.78; 14 CH carbon lines out of the 16 expected for the two isomers were resolved, $\delta$ 125.52, 126.70, 127.41, 127.92, 128.09, 128.92, 129.54, 131.07, 131.12, 131.31, 131.40, 132.96, 133.31, 134.35; both $CH_3$ carbon lines expected for the two isomers (the ratio was about 63:37) were resolved, $\delta$ 19.46, 22.04. Anal. Calcd for $C_{17}H_{13}NO_4S$: C, 62.4; H, 4.0; N, 4.3. Found: C, 62.6; H, 4.2; N, 4.4.

**6-Methyl-2-nitro-3-(phenylsulfonyl)naphthalene (10d).** White solid, mp 269.0−270.3 °C (*p*-xylene/petroleum ether, bp 40−60 °C); $\nu_{max}$ (Nujol) 1617, 1528, 1341, 1307, 1289, 1156, 1145, 1121, 1086 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.64 (3H, s), 7.59 (4H, m), 7.97 (4H, m), 8.37 (1H, s), 8.92 (1H, s); ($CD_3SOCD_3$) $\delta$ 2.59 (3H, s), 7.73 (4H, m), 7.91 (2H, m), 8.19 (2H, m), 8.74 (1H, s), 9.07 (1H, s); $^{13}$C NMR ($CD_3SOCD_3$) $\delta$ 21.38, 125.92,

127.24, 128.81, 128.96, 129.30, 129.50, 131.59, 132.72, 133.58, 133.71, 133.91, 139.84, 141.06, 143.19. Anal. Calcd for $C_{17}H_{13}NO_4S$: C, 62.4; H, 4.0; N, 4.3. Found: C, 62.7; H, 4.1; N, 4.0.

**6-Methoxy-2-nitro-3-(phenylsulfonyl)naphthalene (10e).** Yellowish solid, mp 273.9−275.2 °C (dichloromethane−petroleum ether, bp 80−100 °C); $\nu_{max}$ (Nujol) 1618, 1532, 1502, 1343, 1306, 1252, 1151, 1138, 1119, 1084, 1029 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.02 (3H, m), 7.41 (1H, d, $J$ = 2.2 Hz), 7.45 (1H, dd, $J$ = 2.2 and 9.1 Hz), 7.59 (3H, m), 7.93 (1H, d, $J$ = 9.1 Hz), 8.00 (2H, m), 8.38 (1H, s), 8.90 (1H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 55.83, 107.58, 124.14, 126.46, 127.83, 128.76, 128.87, 130.61, 131.99, 132.94, 133.24, 135.23, 141.27, 146.79, 161.37. Anal. Calcd for $C_{17}H_{13}NO_5S$: C, 59.5; H, 3.8; N, 4.1. Found: C, 59.3; H, 4.0; N, 4.2.

**Methyl 6-Nitro-7-(phenylsulfonyl)naphthalene-2-carboxylate (10f).** Yellowish solid, mp 258.5−259.8 °C (EtOH); $\nu_{max}$ (Nujol) 1709, 1535, 1356, 1326, 1281, 1229, 1158, 1107, 1086 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.05 (3H, s), 7.60 (3H. m), 8.02 and 8.09 [3H in all, partly overlapping m and d ($J$ = 8.8 Hz)], 8.37 and 8.39 [2H in all, partly overlapping d ($J$ = 1.4 Hz) and dd ($J$ = 1.4 and 8.8 Hz)], 8.88 (1H, s), 9.10 (1H, s); $^1H$ NMR (400 MHz, DMF-$d_7$) $\delta$ 4.01 (3H, s), 7.72 (3H, m), 8.13 (2H, m), 8.25 (1H, dd, $J$ = 1.6 and 8.7 Hz), 8.43 (1H, d, $J$ = 8.7 Hz), 8.85 (1H, s), 9.13 (1H, s), 9.47 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 52.92, 125.57, 128.18, 129.08, 129.36, 130.54, 131.91, 132.12, 132.43, 133.69, 135.73, 135.91, 140.75, 165.66; $^{13}C$ NMR (100 MHz, DMF-$d_7$) $\delta$ 58.09, 131.37, 133.58, 135.15, 135.59, 135.79, 136.86, 137.09, 137.96, 138.19, 139.73, 141.97, 142.22, 146.78, 151.58, 171.29. Anal. Calcd for $C_{18}H_{13}NO_6S$: C, 58.2; H, 3.5; N, 3.8. Found: C, 58.3; H, 3.6; N, 3.8.

**3-Nitro-2-(phenylsulfonyl)phenanthrene (10g).** Yellow solid, mp 261.1−262.2 °C (toluene); $\nu_{max}$ (Nujol) 1526, 1504, 1339, 1308, 1239, 1147, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.57 (3H, m), 7.80 (2H, m), 7.96 and 8.04 [5H in all, partly overlapped d ($J$ = 8.8 Hz) and m], 8.64 (1H, m), 9.00 (1H, s), 9.14 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 121.08, 123.47, 126.06, 128.09, 128.51, 129.00, 129.17, 129.29, 129.51, 131.86, 132.10, 132.88, 133.21, 133.33, 133.48, 133.74, 141.09, 145.18. Anal. Calcd for $C_{20}H_{13}NO_4S$: C, 66.1; H, 3.6; N, 3.9. Found: C, 66.0; H, 3.8; N, 3.8.

**2-Nitro-3-(phenylsulfonyl)phenanthrene (10h).** Yellowish solid, mp 318.0−318.6 °C (*p*-xylene); $\nu_{max}$ (Nujol) 1530, 1357, 1318, 1306, 1240, 1154, 1084 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.58 (3H, m), 7.87 (3H, m), 8.05 (4H, m), 8.41 (1H, s), 8.90 (1H, dd, $J$ = 1.2 and 8.4 Hz), 9.78 (1H, s); $^{13}C$ NMR (100 MHz, DMF-$d_7$) $\delta$ 124.93, 126.53, 126.58, 128.73, 129.25, 129.32, 129.93, 129.98, 130.00, 130.08, 131.39, 132.08, 133.48, 133.93, 134.63, 135.38, 141.98, 146.14. Anal. Calcd for $C_{20}H_{13}NO_4S$: C, 66.1; H, 3.6; N, 3.8. Found: C, 66.3; H, 3.8; N, 3.8.

**6-Nitro-5-(phenylsulfonyl)benzo[*b*]thiophene (10i).** Yellow solid, mp 190.1−190.5 °C (toluene/petroleum ether, bp 40−60 °C); $\nu_{max}$ (Nujol) 1550, 1525, 1449, 1356, 1310, 1240, 1205, 1149, 1100, 1065 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.58 [4H in all, partly overlapped m and d ($J$ = 5.5 Hz)], 7.92 (1H, d, $J$ = 5.5 Hz), 8.00 (2H, dd, $J$ = 1.6 and 8.0 Hz), 8.41 (1H, s), 8.91(1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 120.24, 124.75, 127.61, 127.93, 128.93, 131.36, 133.38, 134.07, 141.15, 141.33, 143.48, 144.15. Anal. Calcd for $C_{14}H_9NO_4S_2$: C, 52.6; H, 2.8; N, 4.4. Found: C, 52.5; H, 2.9; N, 4.2.

**5-Nitro-6-(phenylsulfonyl)benzo[*b*]thiophene (10j).** White solid, mp 174.6−175.6 °C (toluene); $\nu_{max}$ (Nujol) 1551, 1521, 1449, 1352, 1310, 1292, 1154, 1123, 1085, 1069 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.57 (4H, m), 7.95 and 8.00 [3H in all, partly overlapping d ($J$ = 5.4 Hz) and m], 8.29 (1H, s), 8.98 (1H, s); $^{13}C$ NMR ($CDCl_3$) $\delta$ 120.48, 124.45, 126.96, 127.98, 128.98, 130.14, 133.44, 135.06, 141.14, 142.14, 142.39, 145.41. Anal. Calcd for $C_{14}H_9NO_4S_2$: C, 52.6; H, 2.8; N, 4.4. Found: C, 52.9; H, 2.9; N, 4.3.

**Acknowledgment.** Financial support was provided by grants from Università di Genova and Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR, PRIN-2001). In the framework of the collaboration for the PRIN-2001 funding, 400-MHz NMR spectra were kindly recorded at the Trieste Research Unit.

JO034264Q