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From β-Nitrothiophenes to Ring-Fused Nitrobenzenes: An Overall Ring-Enlargement Process via a Facile, Aromatization-Driven, Thermal 6π Electrocyclization[1]

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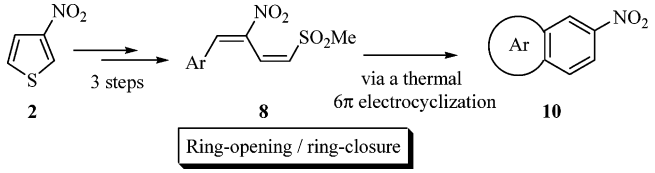

In prosecution of previous work on the thermal cyclization of 1-aryl-4-methanesulfonyl-2-nitro-3-phenylsulfonyl-1,3-butadienes (**7**), the 3-unsubstituted derivatives **8**, deriving from the initial ring opening of 3-nitrothiophene (**2**), have been likewise found herein to undergo cyclization, followed by aromatization, in analogous mild experimental conditions, leading to the ring-fused homo- or heteroaromatic nitro derivatives **10**. The concerted electrocyclic nature of the process is strongly supported by the outcome of tests based on the variation of the polarity of the solvent or of the electron density on the aryl of **8**. Thus, the successful application of the process to the non-phenylsulfonyl-activated **8** significantly widens the scope of a synthetically valuable overall ring-opening/ring-closing procedure from nitrothiophenes. Support to the recently renewed interest in thermal 6π electrocyclizations as a tool for the construction of the benzene ring is furthermore provided.

Introduction

As compared to the photochemical counterpart,[2] notwithstanding an undeniable theoretical significance the thermal 6π electrocyclization has reportedly[3] received little attention as far as its potentialities in organic synthesis are concerned. More recently, though, the interest in the thermal electrocyclization of conjugated trienes for the construction of the benzene ring has found, in particular, renewed strength: this is due to the possibility to exploit the presence of a suitable leaving group (Y) capable of driving the reaction toward aromatization after cyclization of the triene to a cyclohexadiene intermediate (Scheme 1).[4]

In this line, within a long-standing research project on the synthetic exploitation of the versatile butadiene building-blocks deriving from the ring-opening of ni-

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(1) Synthetic Exploitation of the Ring-Opening of Nitrothiophenes, Part XVII. For part XVI, see ref 5a.

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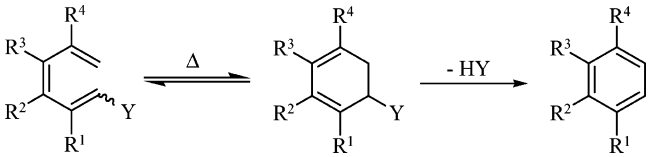
SCHEME 1



trothiophenes with secondary amines,[5] we have recently reported[5b] an appealing access to ring-fused homo- and heteroaromatic derivatives (**9**) from 3-nitro-4-(phenylsulfonyl)thiophene (**1**) (Scheme 2). The final **7** to **9** ring-closure step in the scheme has been interpreted as a 6π electrocyclization followed by methanesulfinic acid elimination from the nonisolated intermediate **11** (X = $PhSO_2$) (Scheme 3). The experimental conditions for the cyclization/aromatization step appear surprisingly mild for a process involving the initial loss of aromaticity of the Ar moiety.[6] Such a mildness has been justified on the grounds (a) of a proper spatial arrangement of **7** [to which the (1*E*,3*E*) configuration[5b] allows the attainment of the s-cis conformation necessary for cyclization][4b] and/or (b) of the cis relation between SO_2Me and the bridgehead H atom in **11** (X = $PhSO_2$),[7] suitable for a concerted syn β-elimination of $MeSO_2H$. The latter process effectively drives the system to the final product with aromatization of the condensed polycycle.

Very recent reports have enlightened (both on experimental[8] and on computational grounds[4b]) the favorable role played by electron-withdrawing groups (such as the phenylsulfonyl group) on the hexatriene chain in lowering the activation-energy barrier for the hexatriene to cyclohexadiene thermal electrocyclization. On the other hand, in the thermal cyclization/aromatization of sulfonyl-activated phenylbutadienes in MeCN in the presence of iodine,[9] the occurrence of an electrocyclic process has been recently questioned in favor of a more classical electrophilic substitution pathway of ionic character.

On these grounds we have extended our methodology to **8**, characterized by a less activated side chain, to verify the feasibility of the cyclization/aromatization process also in less favorable electronic conditions.[4b,8] We have also run suitable tests to support the electrocyclic, nonionic nature of the process. Such goals would definitely contribute to assign to thermal 6π electrocyclizations a more significant role in the panorama of the synthetic methodologies available for the construction of aromatic rings.

Results and Discussion

Compounds **8** have been prepared starting from 3-nitrothiophene (**2**) following a procedure similar to that already described for the synthesis of derivatives **7** from 3-nitro-4-(phenylsulfonyl)thiophene (**1**). The yields of **8** and of the methylthio precursors **6** [Scheme 2, steps c and b, respectively] are reported in Table 1,[10] together with the experimental details relevant to the thermal treatment of **8** in the same conditions previously reported for the phenylsulfonyl derivatives **7**.[5b] In the last column of the table, yields and reaction times for the cyclization of the latter compounds[5b] are also reported, for comparison sake.

The nitrobutadienes **8a**−**i** actually undergo, much as the phenylsulfonyl-activated counterparts **7**, a thermal intramolecular cyclization to yield benzocondensed homo- or heteroaromatic systems (Chart 1) as a consequence of the neat loss of methanesulfinic acid. The data in Table 1 bring to evidence that the reaction on **8** is generally characterized by appreciably longer times and/or sizably lower yields of isolated products. Some degradation at the experimental temperature is partly responsible for the latter result, as can be deduced when confronting the final yields with those based on the consumed substrate after quenching before completion in some representative cases (namely **8a**, **8d**, and **8f**: cf. footnotes *g*, *j*, and *m* of Table 1, respectively). Nonetheless, even if some time-dependent yield reduction of **5b** is allowed for, the overall comparison between the **7** to **9** and the **8** to **10** transformations definitely enlightens a significant favorable effect played by the $PhSO_2$ group in the cyclization of **7**.

Although such an outcome is well in line with the cited recent reports[4b,8] on the role played by electron-withdrawing groups on thermal electrocyclizations, the onset of sizable electronic effects could cast some doubts on the real pericyclic nature of the cyclization step in favor of the participation of some ionic component. Actually, an electrophilic-aromatic-substitution component has already been proposed,[11] and recently reaffirmed to justify the effect of substituents on the phenyl ring, within the thermal cyclization/aromatization process on sulfonyl-activated phenylbutadienes in MeCN in the presence of iodine.[9] Furthermore, as already pointed out,[5b] an aspect of our system that is surely intriguing is represented by the mildness of the experimental conditions (reflux in

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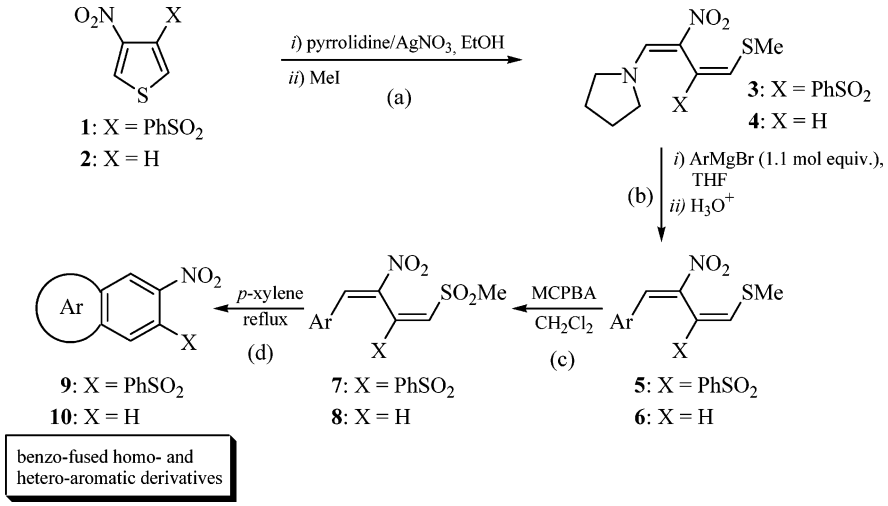
SCHEME 2



SCHEME 3

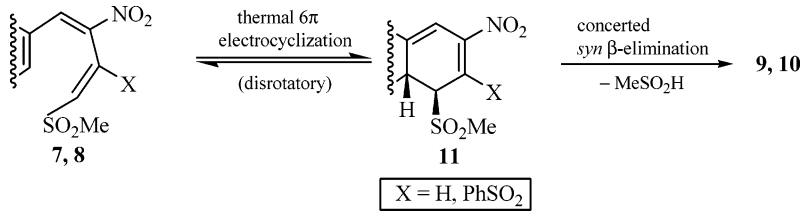


TABLE 1. Experimental Details for Steps b, c, and d of Scheme 2 for X = H[n]

Ar	**6**[a,b]	**8**[a,c]	**10**[a,d] (reaction time)[e]	**9**[d,f] (reaction time)
Ph	**6a**: 90%	**8a**: 92%	**10a**: 86% (96 h)[g]	**9a**: 96% (48 h)
2-MeC_6H_4	**6b**: 95%	**8b**: 94%	**10b**: 90% (80 h)	**9b**: 98% (24 h)
3-MeC_6H_4	**6c**: 88%	**8c**: 93%	**10c**−**10c′**: 79% (90 h)[h]	**9c**−**9c′**: 93% (17 h)[i]
4-MeC_6H_4	**6d**: 98%	**8d**: 98%	**10d**: 84% (90 h)[j]	**9d**: 98% (24 h)[k]
3-$MeOC_6H_4$	**6e**: 87%	**8e**: 96%	**10e**−**10e′**: 92% (90h)[l]	
1-naphthyl	**6f**: 91%	**8f**: 98%	**10f**: 77% (3.5 h)[m]	**9f**: 88% (1.5 h)
2-naphthyl	**6g**: 89%	**8g**: 98%	**10g**: 75% (1 h)	**9g**: 98% (1 h)
2-thienyl	**6h**: 76%	**8h**: 92%	**10h**: 90% (20 h)	**9h**: 90% (20 h)
3-thienyl	**6i**: 78%	**8i**: 93%	**10i**: 72% (20 h)	**9i**: 98% (16 h)

[a] Isolated yields. [b] [**4**]: ca. 0.08 M in THF. ArMgBr: 1.1 mol equiv; 0 °C; H_3O^+ quenching. [c] [**6**]: 0.07 M in CH_2Cl_2. *m*-Chloroperbenzoic acid: 2 mol equiv; rt. [d] [Substrate]: 5×10^{-3} M in dry *p*-xylene; reflux. [e] Reaction driven to completion and followed by monitoring (TLC) the disappearance of substrate. The reported times should be regarded as only indicative. [f] Data from ref 5b. [g] The yield is 72% after 48 h (88% on the reacted substrate). [h] Mixture of isomeric **10c** and **10c′** in a 57/43 molar ratio (^{1}H NMR analysis), from which only **10c** could be separated in pure form. [i] Mixture of isomeric **9c** and **9c′** in a 66/34 molar ratio (^{1}H NMR analysis).[5b] [j] The yield is 73% after 70 h (90% on the reacted substrate). [k] Optimized conditions and final-point detection with respect to the previous report (ref 5b). [l] Mixture of isomeric **10e** and **10e′** in a 81/19 molar ratio (^{1}H NMR analysis). [m] The yield is 67% after 1.5 h (83% on the reacted substrate). [n] The results for the cyclization/aromatization of compounds **7**[5b] are also reported in the last column for comparison sake.

p-xylene) necessary to perform the cyclization on compounds **7** or **8** as compared to typical literature examples where electron couples of an aromatic sextet are similarly involved in an electrocyclization.[2,6] For instance, the thermal benzocyclization of 1-aryl-1,3-butadienes until recently has been reported to occur in much harsher conditions such as flash vacuum pyrolysis,[6b−d] otherwise acidic catalysis[6a] or photostimulation[6e] can be employed. On these grounds, the successful extension of the process to compounds **8**, i.e. in the absence of the activating $PhSO_2$ group, under the same mild conditions applied to **7** seems even more surprising and therefore deserving of some kind of confirmation for the occurrence of a concerted pericyclic mechanism.

Clues on the intervention of ionic pathways can possibly be traced by means of the use of solvents of different polarity and/or the introduction in the aromatic moiety of groups characterized by strong electronic effects, to cause appreciable variations in the electron density on the aromatic ring itself.

Parallel tests have been carried out on **8a** at reflux in benzene and in acetonitrile, i.e., in two solvents with very similar boiling points (80 and 81 °C, respectively) but with completely different physical properties (benzene: E_T^N 0.111, A_j 0.15, B_j 0.59, ϵ_r 2.27; acetonitrile: E_T^N 0.460, A_j 0.37, B_j 0.86, ϵ_r 35.94).[12] In a first experiment the reaction mixtures have been refluxed for the time (96 h) necessary to guarantee completion of the reaction in *p*-xylene (see Table 1), observing a conversion (deter-

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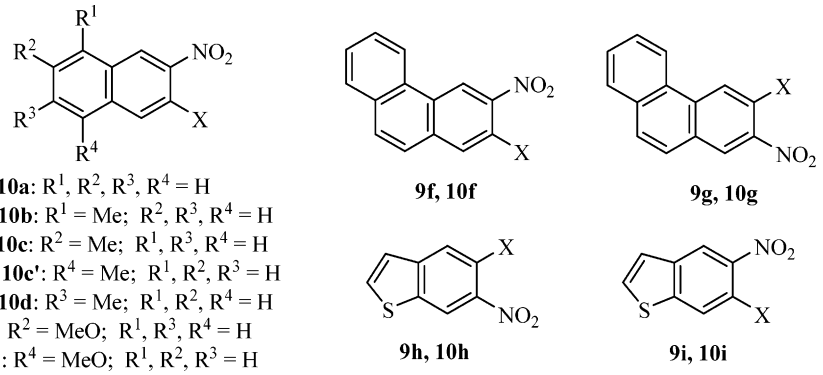
CHART 1



9a, 10a: R^1, R^2, R^3, R^4 = H
9b, 10b: R^1 = Me; R^2, R^3, R^4 = H
9c, 10c: R^2 = Me; R^1, R^3, R^4 = H
9c', 10c': R^4 = Me; R^1, R^2, R^3 = H
9d, 10d: R^3 = Me; R^1, R^2, R^4 = H
10e: R^2 = MeO; R^1, R^3, R^4 = H
10e': R^4 = MeO; R^1, R^2, R^3 = H

9f, 10f **9g, 10g**

9h, 10h **9i, 10i**

mined by ^{1}H NMR) of approximately 4 ± 1% and 8 ± 1% in benzene and in acetonitrile, respectively. The 4% conversion in the former solvent, compared to the 100% conversion in *p*-xylene after the same time, is perfectly in line with the fact that benzene and *p*-xylene show similar physical properties but very different boiling points [Δ(bp): 58 °C]. Interestingly, the reactivity difference between benzene and MeCN is significant but seemingly not high enough to justify the involvement of ionic intermediates. In a second experiment, where the reaction time was prolonged to 19 days, 23% and 27% of **10a** was isolated from the two solvents, with an overall balance of 98% and 87% (23% and 31% of conversion), respectively: thus, only a meagre, although sizable, favorable effect played by the solvent polarity is definitely reaffirmed on more sound quantitative grounds.

As far as the electronic effects on the aryl moiety of the substrate are concerned, the completion of the cyclization/aromatization process on **8e**, which contains the strongly electron-donating methoxy group, required 4 days, leading to an overall 92% yield of **10e** and **10e′** (see Table 1). These results are closely comparable with those for either the parent phenyl derivative **8a** or the 3-methyl derivative **8c** and thus definitely exclude any significant concurrence of an aromatic electrophilic substitution pathway. For comparison sake, a 3-methoxy group on the aromatic moiety has been shown to play a strong (>15-fold) accelerative effect in the previously cited cyclization of 1-aryl-1,3-butadienes in MeCN/I_2, to support the proposed ionic pathway.[9]

As a matter of fact, rather than by the electronic density on the Ar moiety of the substrate, the reaction herein is clearly influenced by the aromaticity[13] of the homo- or heteroring that participates in the cyclization. Thus, while for the phenyl compounds **a**−**e** the indicative reaction times based on the disappearance of substrate vary within very narrow ranges around mean values of 24 and 90 h for **7** and **8**, respectively, the cyclization step is sizably faster for the naphthyl or the thienyl derivatives **f**−**i**; such a higher reactivity is coupled with a higher similarity in the behavior between **7** and **8**, although the latter still led to somewhat lower yields.

As a final comment, the reaction times relevant to the derivatives **f** and **g** reveal the occurrence of a significant steric effect (likely due to the *peri* hindrance) that conversely could not be observed in the case of the thienyl derivatives **h** and **i**, for which different steric requirements are not expected.

Conclusions

Experimental tests devised to bring to evidence the involvement of pathways of ionic nature for the intramolecular cyclization step of the overall **8** to **10** transformation of Scheme 1 have altogether furnished an essentially negative response. Thus, the results reported herein seem to reasonably confirm the previously advanced[5b] 6π electrocyclic nature of a process that reveals on the other hand to be surprisingly facile most likely because of a subsequent favorable aromatization via a concerted syn β-elimination of methanesulfinic acid. The successful extension of the process to the non-phenylsulfonyl-activated compounds **8** is particularly interesting from a synthetic point of view. As a matter of fact, the result significantly widens the range of applicability of the process and thus adds on to the recently renewed interest in thermal electrocyclizations[4,8] as a valuable tool in homo- and heterocyclic synthesis. Actually, besides the undoubtedly interesting mechanistic aspects, the system herein is definitely endowed with the practical advantage of providing a relatively mild access to variously functionalized ring-fused homo- or heteroaromatic nitro compounds which generally cannot be achieved other than with rather long and tedious syntheses, often characterized by very low overall yields.

The overall ring-opening/ring-closure process can also be envisaged as a ring enlargement, which leads from nitrothiophenes to ring-fused nitrobenzenes via extrusion of the sulfur atom and uptake of two carbons from the Ar moiety to build the final nitrobenzene ring.

Experimental Section

Reactions of 4 with Aromatic Organometallic Reagents. The reactions were typically performed on 0.5 g (2.33 mmol) of substrate, following the procedure previously reported for the synthesis of **6d**.[10b] Yields of compounds **6a**−**i** are collected in Table 1.

(1*E*,3*Z*)-(4-Methylsulfanyl-2-nitrobuta-1,3-dien-1-yl)-benzene (6a). Yellow solid, mp 85.7−86.8 °C (ethanol); ν_{max} (Nujol) 1630, 1570, 1309 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25 (3H, s), 6.46 (1H, d, *J* = 10.4 Hz), 6.61 (1H, d, *J* = 10.4 Hz), 7.36−7.45 (3H, m), 7.51−7.59 (2H, m), 8.05 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.6, 114.3, 128.8, 130.6, 130.8, 131.4, 134.4, 139.0, 145.0.

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Anal. Calcd for $C_{11}H_{11}NO_2S$ (221.28): C, 59.71; H, 5.01; N, 6.33. Found: C, 59.82; H, 5.10; N, 6.19.

***(1E,3Z)*-1-(4-Methylsulfanyl-2-nitrobuta-1,3-dien-1-yl)-naphthalene (6f).** Yellow oil. ν_{max} (neat) 3049, 2921, 1688, 1630, 1572, 1513, 1460, 1433, 1399, 1319, 1245, 1004 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (3H, s), 6.35 (1H, d, J = 10.6 Hz), 6.45 (1H, d, J = 10.6 Hz), 7.32−7.58 (4H, m), 7.72−7.87 (2H, m), 7.92−8.02 (1H, m), 8.60 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.6, 113.7, 123.6, 125.04, 126.2, 126.9, 127.4, 128.5, 128.7, 130.8, 131.4, 131.6, 133.3, 138.2, 146.3. Anal. Calcd for $C_{15}H_{13}NO_2S$ (271.33): C, 66.40; H, 4.83; N, 5.16. Found: C, 66.53; H, 4.89; N, 5.11.

***(1E,3Z)*-2-(4-Methylsulfanyl-2-nitrobuta-1,3-dien-1-yl)-thiophene (6h).** Orange solid, mp 49.1−50.0 °C (light petroleum/toluene); ν_{max} (Nujol) 1617, 1575, 1414, 1291, 1251, 1073, 1052, 1024 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.34 (3H, s), 6.32 (1H, d, J = 10.2 Hz), 6.75 (1H, d, J = 10.2 Hz), 7.15 (1H, dd, J = 5.1 and 3.6 Hz), 7.46 (1H, d, J = 3.6 Hz), 7.62 (1H, d, J = 5.1 Hz), 8.27 (1H, s); ^{13}C NMR ($CDCl_3$) δ 17.3, 113.9, 127.9, 128.4, 133.2, 134.3, 135.7, 141.5, 142.2. Anal. Calcd for $C_9H_9NO_2S_2$ (227.30): C, 47.56; H, 3.99; N, 6.16. Found: C, 47.78; H, 3.92; N, 6.13.

Oxidation of Compounds 6 to 8. The reactions were performed on 2 mmol of the appropriate substrate, according to the conditions previously described.[5b] Relevant yields are reported in Table 1.

***(1E,3Z)*-(4-Methanesulfonyl-2-nitrobuta-1,3-dien-1-yl)-benzene (8a).** Yellow solid, mp 146.6−147.8 °C (ethanol); ν_{max} (Nujol) 1657, 1596, 1516, 1327, 1311, 1299, 1212, 1192, 1157, 1139, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.98 (3H, s), 6.78 (1H, d, J = 11.3 Hz), 6.95 (1H, dd, J = 11.3 and 1.5 Hz), 7.45−7.53 (5H, m), 8.18 (1H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 41.4, 129.2, 130.5, 130.6, 131.3, 131.8, 135.9, 137.7, 141.7. Anal. Calcd for $C_{11}H_{11}NO_4S$ (253.27): C, 52.16; H, 4.38; N, 5.53. Found: C, 52.09; H, 4.22; N, 5.63.

***(1E,3Z)*-1-(4-Methanesulfonyl-2-nitrobuta-1,3-dien-1-yl)naphthalene (8f).** Yellow solid, mp 131.3−132.8 °C (toluene/petroleum ether); ν_{max} (Nujol) 1620, 1510, 1301, 1137 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.99 (3H, s), 6.67 (1H, d, J = 11.4 Hz), 6.80 (1H, dd, J = 11.4 and 1.8 Hz), 7.46−7.70 (4H, m), 7.87−8.04 (3H, m), 8.86 (1H, s); ^{13}C NMR ($CDCl_3$) δ 41.3, 123.8, 125.2, 127.1, 127.7, 127.8, 129.0, 130.1, 130.4, 131.5, 132.3, 133.4, 135.3, 136.0, 143.8. Anal. Calcd for $C_{15}H_{13}NO_4S$ (303.33): C, 59.39; H, 4.32; N, 4.62. Found: C, 59.28; H, 4.37; N, 4.78.

***(1E,3Z)*-2-(4-Methanesulfonyl-2-nitrobuta-1,3-dien-1-yl)thiophene (8h).** Yellow solid, mp 162.9−164.1 °C (ethanol); ν_{max} (Nujol) 1647, 1598, 1497, 1323, 1299, 1185, 1139, 1058 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.02 (3H, s), 6.84 (1H, d, J = 11.2 Hz), 7.05 (1H, dd, J = 11.2 and 1.5 Hz), 7.22 (1H, dd, J = 5.0 and 3.8 Hz), 7.52 (1H, d, J = 3.8 Hz), 7.74 (1H, d, J = 5.0 Hz), 8.37 (1H, s); ^{13}C NMR (CD_3COCD_3) δ 41.9, 129.6, 129.8, 130.2, 135.0, 135.6, 137.7, 138.9, 140.3. Anal. Calcd for $C_9H_9NO_4S_2$ (259.30): C, 41.69; H, 3.50; N, 5.40. Found: C, 41.87; H, 3.33; N, 5.34.

Thermal Cyclization of Compounds 8 to 10.[5b] In a flask the appropriate substrate (1 mmol) was dissolved in dry *p*-xylene (200 mL) and the solution was refluxed until TLC showed complete disappearance of the substrate (1−98 h). The solvent was then evaporated under reduced pressure and the residue purified by column chromatography and/or by crystallization. Yields are reported in Table 1.

2-Methyl-7-nitronaphthalene (10c)[14] **and 1-Methyl-6-nitronaphthalene (10c′).**[15] The crude product (0.148 g, 79%) from the cyclization of **8c** was a chromatographically unseparable mixture of **10c** (0.084 g, 45%) and **10c′** (0.064 g, 34%) (as deduced by ^1H NMR). Compound **10c** could be isolated by crystallization as a pale yellow solid, mp 99.9−101.0 °C (ethanol) [lit.[14] mp 105 °C]; ^1H NMR ($CDCl_3$) δ 2.57 (3H, s), 7.53 (1H, d, J = 8.4 Hz), 7.80 (1H, s), 7.85 (1H, d, J = 8.4 Hz), 7.91 (1H, d, J = 8.8 Hz), 8.17 (1H, dd, J = 8.8 and 2.1 Hz), 8.72 (1H, d, J = 2.1 Hz). ^1H NMR signals of compounds **10c′** could be deduced by the mixture spectrum: ^1H NMR ($CDCl_3$) δ 2.75 (3H, s), 7.51−7.56 (2H, m), 7.89 (1H, d, J = 9.6 Hz), 8.11 (1H, d, J = 9.4 Hz), 8.26 (1H, dd, J = 9.4 and 2.4 Hz), 8.79 (1H, d, J = 2.4 Hz).

2-Methoxy-7-nitronaphthalene (10e).[16] Yellow solid (0.152 g, 75%), mp 111.5−111.8 °C (ethanol); ν_{max} (Nujol) 1629, 1610, 1523, 1397, 1343, 1263, 1222, 1199, 1181, 1145, 1086, 1033 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.97 (3H, s), 7.29 (1H, d, J = 2.6 Hz), 7.34 (1H, dd, J = 2.6 and 9.2 Hz), 7.84 (1H, d, J = 9.2 Hz), 7.88 (1H, d, J = 9.0 Hz), 8.10 (1H, dd, J = 9.0 and 2.4 Hz), 8.70 (1H, d, J = 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 55.5, 107.3, 117.1, 122.8, 123.2, 129.1, 129.4, 131.4, 133.5, 146.1, 159.0. Anal. Calcd for $C_{11}H_9NO_3$ (203.19): C, 65.02; H, 4.46; N, 6.89. Found: C, 65.09; H, 4.41; N, 6.99.

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Supporting Information Available: General experimental information and physical, microanalytical, and/or spectroscopic characterization of all the reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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