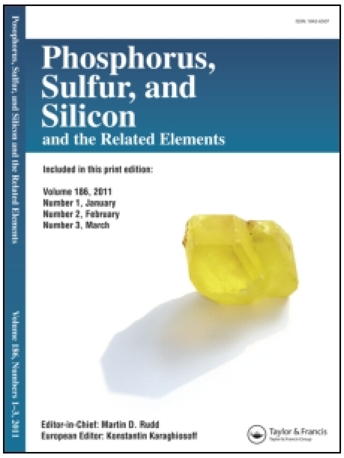

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REACTIVITY OF BIFUNCTIONAL ALKENES WITH DIAZOMETHANE

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REACTIVITY OF BIFUNCTIONAL ALKENES WITH DIAZOMETHANE

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The cycloaddition of diazomethane to 1-aroyl-2-arylsulfonylethenes (**1**) and 1,2-bis (arylsulfonyl) ethenes (**IV**) under different conditions led to a variety of pyrazolines and pyrazoles. The reactivity of pyrazolines was also studied by pyrolysis, nitrosation and acylation.

Keywords: 1-Aroyl-2-arylsulfonylethenes; 1,2-bis(arylsulfonyl)ethenes; 2-pyrazolines; pyrazoles; cyclopropanation

INTRODUCTION

The chemistry of five membered heterocycles containing sulfur and nitrogen has gained importance mainly due to their varied physiological action and diverse physico-chemical properties[1–5]. Among them, pyrazole and its derivatives possess a wide spectrum of biological properties. During the last one and half decades, we have been extensively investigating the synthetic potential of activated alkenes as a source for a variety of heterocyclic systems[6–10]. In fact, 1,3-dipolar cycloaddition of ylide to an alkene involving 3+2 principle-addition of diazomethane to activated alkenes, is a facile route for 2-pyrazolines. This principle has been adopted to study the reactivity of bifunctional alkenes in this communication.

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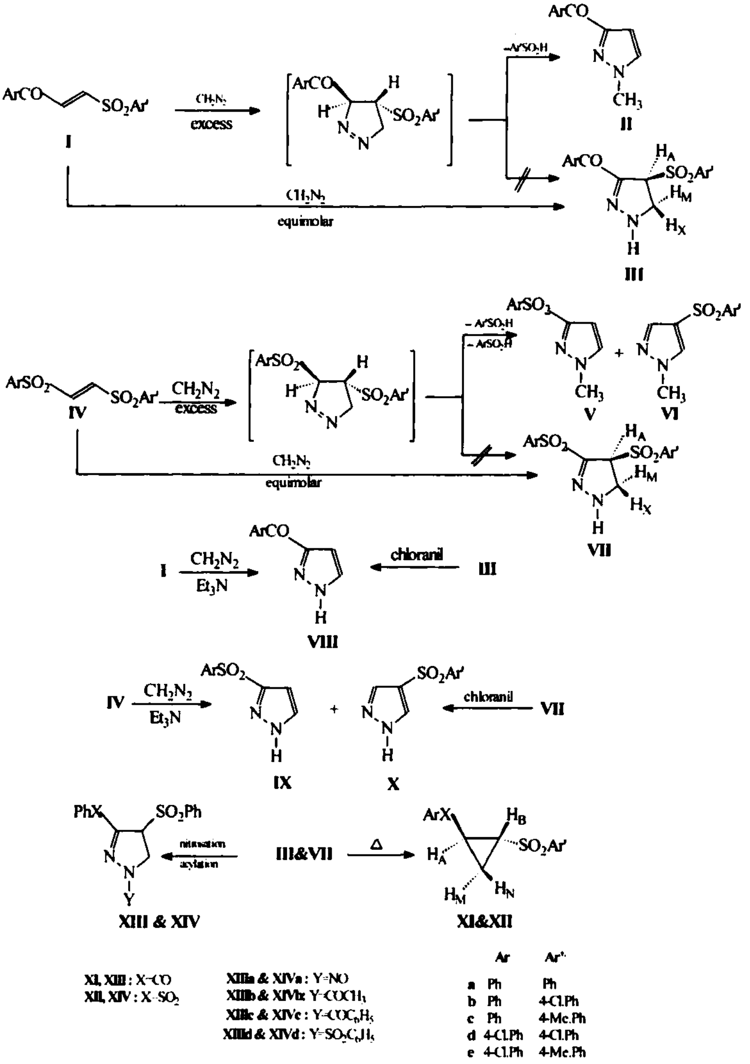
RESULTS AND DISCUSSION

The synthetic scheme involves treatment of 1-aroyl-2-arylsulfonylethenes (**1**) with excess diazomethane and keeping it overnight. The product formed after work up was found to be N-methyl-3-aroylpyrazole (**II**) instead of the expected product, 3-aroyl-4-arylsulfonyl-2-pyrazoline (**III**). This may be due to the loss of arylsulfinic acid from the intermediate adduct. Further, the excess diazomethane might be responsible for N-methylation. The ^{1}H NMR spectra of **II** displayed two doublets for methine protons at C-4 and C-5 in the regions 7.58–7.62 and 6.65–6.72 ppm, respectively. Likewise, when diazomethane was added to 1,2-bis(arylsulfonyl)ethenes (**IV**), a mixture of products, N-methyl-3-arylsulfonylpyrazoles (**V**) and N-methyl-4-arylsulfonyl pyrazoles (**VI**) were obtained instead of 3,4-bis(arylsulfonyl)-2-pyrazolines (**VII**). The ratio of the products formed depends on the direction of loss of arylsulfinic acid from the initial adduct.

The reaction was repeated with equimolar ratio of diazomethane and **I**. After 6 h the indication of product formation was observed in TLC and the compound isolated was identified as 3-aroyl-4-arylsulfonyl-2-pyrazolines (**III**) by spectral parameters. However, when the same reaction was carried out with **IV**, the solution became colourless after 2 h and the product obtained when analysed was found to be **VII**. The ^{1}H NMR spectra of **III** and **VII** indicated AMX splitting pattern for methine and methylene protons of pyrazoline ring. The H_A (4.52–4.85, J_{AM} = 12.61–12.64, J_{AX} = 5.54–5.55) absorbed at downfield compared to H_M (3.64–3.95, J_{MX} = 9.98–10.01) and H_X(3.35–3.60). Among H_M and H_X, the former showed a signal at downfield region than H_X due to the deshielding effect of the arylsulfonyl moiety. The J values indicate that H_A, H_M and H_A, H_X are *cis* and *trans* oriented, respectively, while H_M, H_X are *geminal*. Further when the reaction was carried out with an equimolar ratio of diazomethane and **I** in the presence of a base, triethylamine, and kept for 24–30 h, 3-aroylpyrazoles (**VIII**) were obtained. However with **IV**, a mixture of 3-arylsulfonyl/4-arylsulfonylpyrazoles (**IX** & **X**), resulted. These compounds were also formed when **III** and **VII** were subjected to the reaction with chloranil. The ^{1}H NMR spectra of **VIII** and **IX** showed two doublets for methine protons at C-4 and C-5 of pyrazoline ring at 7.98–8.05 and at 6.78–6.85 ppm. The **X** exhibited two singlets for the protons of C-3 and C-5 at 7.52-.7.61 and at 6.87–6.91 ppm, respectively. The formation of products **II, V, VI** & **VIII** – **X** are contrary to our earlier reports[6,1,12].



SCHEME

Among the most familiar reactions of pyrazolines, elimination of both nitrogen atoms seems to be quite interesting, since their decomposition results cyclopropanes as the major product apart from other minor ones of less importance[6,13]. Thus, the pyrolysis of **III** and **VII** gave

1-aroyl-2-arylsulfonylcyclopropanes (**XI**) and 1,2-bis(arylsulfonyl)-cyclopropanes (**XII**) respectively. The methine and methylene protons of cyclopropane ring in **XI** exhibited ABMN splitting pattern. As a result of *vicinal* and *geminal* couplings each proton appears as a doublet of double doublet (ddd). Thus, the δ_H values at 2.68–2.75, 2.58–2.65, 1.84–1.89 and 1.39–1.45 ppm are assigned to H_A, H_B, H_M and H_N, respectively. The coupling constants of these protons are J_{AB} = 5.72–5.74, J_{AM} = 8.55–8.59, J_{AN} = 6.58–6.59, J_{BM} = 5.55–5.57, J_{BN} = 10.12–10.14 and J_{MN} = 4.64–4.66 Hz, thus shows $H_AH_B = H_BH_M = H_AH_N$ = *trans*, $H_AH_M = H_BH_N$ = *cis* and H_MH_N = *geminal*. However the methine and methylene protons in **XII** exhibited two multiplets at 3.50–3.58 and 2.85–3.00 ppm, respectively. The formation of 2-pyrazolines was also ascertained by their N-substituted derivatives. The nitrosation and acylation of **IIIa** and **VIIa** furnished N-nitroso, N-acetyl, N-benzoyl and N-benzenesulfonyl 2-pyrazolines, **XIIIa-d, XIVa-d**, respectively. Thus the reaction of 1-aroyl-2-arylsulfonylethenes (**I**) and 1,2-bis (arylsulfonyl)ethenes (**IV**) with diazomethane lead to different products depending upon the reaction conditions.

EXPERIMENTAL

Melting points were determined on a Mel.-Temp apparatus and are uncorrected. IR spectra (KBr-disc) were recorded on a Beckmann IR-18 spectrophotometer. NMR spectra were recorded in $CDCl_3$ using 200 MHz on a Bruker spectrospin varian EM-360 spectrophotometer using TMS as a standard. Microanalyses were obtained from the University of Pune, Pune, India. The starting materials **I** and **IV** were prepared as per literature procedure[14].

General Procedure for the Preparation of N-methyl-3-aroylpyrazole (II) / N-Methyl-3/4-arylsulfonylpyrazole (V/VI)

To 5.0 mmol of **I/IV** in 20 ml of dichloromethane, 20 ml of 1.0 M ethereal diazomethane was added at 0°C. The reaction mixture was allowed to stand overnight at 0°C. The solvent was removed under reduced pressure. The product obtained in **I** was purified by column chromatography. However, in **IV** the two products formed were separated and purified by column chromatography. **IIa,b,c** (72, 76, 73%) m.p. 135–136°C (Found: C, 70.85, H, 5.50; N, 15.16. $C_{11}H_{10}N_2O$ requires C, 70.95; H, 5.41; N, 15.04%). ν_{max} (KBr)/cm^{-1} 1540 (C=N), 1620 (CO). δ_H (200 MHz; $CDCl_3$) 3.94 (s, 3H, $C\underline{H}_3$), 6.72 (d, 1H, C_5-$\underline{H}$), 7.58 (d, 1H, C_4-$\underline{H}$), 6.98–7.54 (m, 5H, Ar$\underline{H}$) **IId,e** (82, 75%) m.p. 142–143°C (Found: C, 59.65; H, 4.01; N, 12.60. $C_{11}H_9ClN_2O$ requires C, 59.87; H, 4.11; N, 12.69%). ν_{max}(KBr)/cm^{-1} 1545 (C=N), 1640 (CO). δ_H (200 MHz; $CDCl_3$) 3.97 (s, 3H, $C\underline{H}_3$), 6.65 (d, 1H, C_5-$\underline{H}$), 7.62 (d, 1H, C_4-$\underline{H}$), 6.92–7.41 (m, 4H, Ar$\underline{H}$). **Va,b,c** (46, 55, 54%) m.p. 101–102°C (Found: C, 54.00; H, 4.50; N, 12.50. $C_{10}H_{10}N_2O_2S$ requires C, 54.04; H, 4.53; N, 12.60%). ν_{max}(KBr)/cm^{-1} 1340, 1150 (SO_2), 1550 (C=N). δ_H (200 MHz; $CDCl_3$) 4.00 (s, 3H, $C\underline{H}_3$), 6.84 (s, 1H, C_5-$\underline{H}$), 6.94–7.42 (m, 5H, Ar$\underline{H}$). **Vd,e** (52, 42%) m.p. 98–99°C (Found: C, 46.60; H,3.58; N, 10.96. $C_{10}H_9ClN_2O_2S$ requires C, 46.78; H, 3.53; N, 10.91%). ν_{max} (KBr)/cm^{-1} 1350, 1145 (SO_2), 1560 (C=N). δ_H (200 MHz; $CDCl_3$) 3.98 (s, 3H, $C\underline{H}_3$) 6.86 (s, 1H, C_5-$\underline{H}$), 7.49 (s, 1H, C_4-$\underline{H}$), 6.98–7.45 (m, 4H, Ar$\underline{H}$). **VIa** (50%) m.p. 107–108°C (Found: C, 54.00; H, 4.50; N, 12.50. $C_{10}H_{10}N_2O_2S$ requires C, 54.04; H, 4.53; N, 12.60%). ν_{max}(KBr)/cm^{-1} 1350, 1150 (SO_2), 1540 (C=N). δ_H (200 MHz; $CDCl_3$) 3.89 (s, 3H, $C\underline{H}_3$), 6.95 (s, 1H, C_5-H), 7.48 (s, 1H, C_3-$\underline{H}$), 6.98–7.42 (m, 5H, Ar$\underline{H}$). **VIb,d** (40, 47%) m.p. 114–115°C (Found: C, 46.56; H, 3.48; N, 11.98. $C_{10}H_9Cl_2N_2O_2S$ requires C, 46.78; H, 3.53; N, 11.91%). ν_{max} (KBr)/cm^{-1} 1360, 1140 (SO_2), 1560 (C=N). **VIc,e** (44, 56%) m.p. 95–96°C (Found: C, 55.98; H, 5.08; N, 11.91. $C_{11}H_{12}N_2O_2S$ requires C, 55.91; H, 5.11; N, 11.85%). ν_{max} (KBr)/cm^{-1} 1355, 1160 (SO_2), 1555 (C=N). δ_H (200 MHz; $CDCl_3$) 2.24 (s,3H, Ar$C\underline{H}_3$), 3.85 (s, 3H, $C\underline{H}_3$), 6.96 (s, 1H, C_5-$\underline{H}$), 7.46 (s, 1H, C_3-$\underline{H}$), 6.99–7.44 (m, 4$\underline{H}$, Ar-$\underline{H}$).

General Procedure for the Preparation of 3-aroyl-4-arylsulfonyl-2-pyrazoline (III) / 3,4-bisarylsulfonyl-2-pyrazoline (VII)

To 5.0 mmol of **I/IV** in 20 ml of dichloromethane, 20 ml of 0.5 M ethereal diazomethane was added at 0°C and kept aside at the same temperature. The reaction mixture was monitored by TLC at frequent intervals. After completion of the reaction the solvent was removed with rotary evaporator. The resulting gummy product when passed through a column of silica gel (60–120 mesh, ether-hexane 2:3) gave analytically pure **III/VII. IIIa**

(82%) m.p. 162–164°C (Found: C, 61.32; H, 4.53; N, 8.73. $C_{16}H_{14}N_2O_3$ requires C, 61.13; H, 4.48; N, 8.91%). ν_{max} (KBr)/cm^{-1} 1330, 1120 (SO_2), 1540 (C=N), 1630 (CO), 3350 (NH). δ_H (200 MHz; $CDCl_3$) 3.46 (dd, 1H, H_X), 3.68 (dd, 1H, H_M, J_{MX} = 10.00), 4.64 (dd, 1H, HA, J_{AM}=12.62, J_{AX}=5.54), 6.48 (s, 1H, N$\underline{H}$), 7.02–7.60 (m, 10H, ArH). **IIIb** (85%) m.p. 174–175°C (Found: C, 55.32; H, 3.87; N, 7.86. $C_{16}H_{13}ClN_2O_3S$ requires C, 55.09; H, 3.75; N, 8.03%). ν_{max} (KBr)/cm^{-1} 1335, 1130 (SO_2), 1560 (C=N), 1660 (CO), 3370 (NH). δ_H (200 MHz; $CDCl_3$) 3.55 (dd, 1H, H_X), 3.90 (dd, 1H, H_M, J_{MX}=9.98), 4.52 (dd, 1H, H_A, J_{AM}=12.64, J_{AX}=5.54), 6.45 (s, 1H, N$\underline{H}$) 6.98–7.52 (m, 9H, Ar$\underline{H}$). **IIIc** Yield (78%) m.p. 145–146°C (Found: C, 62.37; H, 4.76; N, 8.65. $C_{17}H_{16}N_2O_3S$ requires C, 62.17; H, 4.91; N, 8.53%). ν_{max} (KBr)/cm^{-1} 1340, 1130 (SO_2), 1555 (C=N), 1640 (CO), 3345 (NH). **IIId** (86%) m.p. 153–154°C (Found: 50.00; H, 3.10; N, 7.45. $C_{16}H_{12}Cl_2N_2O_3S$ requires C, 50.14; H, 3.15, N, 7.30%). ν_{max} (KBr)/cm^{-1} 1320, 1140 (SO_2), 1570 (C=N), 1665 (CO), 3370 (NH). **IIIe** (75%) m.p. 169–170°C (Found: C 56.40; H, 4.26; N, 7.79. $C_{17}H_{15}ClN_2O_3S$ requires C, 56.27, H, 4.16; N, 7.72%). ν_{max} (KBr)/cm^{-1}1340, 1120 (SO_2), 1560 (C=N), 1655 (CO), 3355 (NH). δ_H (200 MHz; $CDCl_3$) 3.58 (dd, 1H, H_X), 3.64 (dd, 1H, HM, J_{MX}=10.01), 4.72 (dd, 1H, HA, J_{AM}=12.62, J_{AX}=5.55), 6.45 (s, 1H, N$\underline{H}$), 7.01–7.55 (m, 8H, Ar$\underline{H}$). **VIIa** (78%) m.p. 142–144°C (Found: C, 51.52; H, 4.00; N, 8.09. $C_{15}H_{14}N_2O_4S_2$ requires C, 51.41; H, 4.02; N, 7.99%). ν_{max} (KBr)/cm^{-1} 1330, 1150 (SO_2), 1560 (C=N), 3360 (NH). δ_H (200 MHz; $CDCl_3$) 3.52 (dd, 1H, H_X), 3.84 (dd, 1H, HM, J_{MX}=10.00), 4.74 (dd, 1H, H_A, J_{AM}=12.62, J_{AX}=5.55), 6.52 (s, 1H, N$\underline{H}$), 7.04–7.56 (m, 10H, Ar$\underline{H}$). **VIIb** (82%) m.p. 135–136°C (Found: C, 46.61; H, 3.49; N, 7.35 $C_{15}H_{13}ClN_2O_4S_2$ requires C, 46.81; H, 3.40; N, 7.29%). ν_{max} (KBr)/cm^{-1} 1340, 1160 (SO_2), 1570 (C=N), 3365 (NH). **VIIc** (85%) m.p. 129–130°C (Found: C, 52.87; H, 4.46; N, 7.56. $C_{16}H_{16}N_2O_4S_2$ requires C, 52.73; H, 4.42; N, 7.68%). ν_{max} (KBr)/cm^{-1} 1335, 1150 (SO_2), 1565 (C=N), 3350 (NH). δ_H (200 MHz; $CDCl_3$) 2.23 (s, 3H, ArC$\underline{H}_3$) 3.35 (dd, 1H, H_X), 3.95 (dd, 1H, H_M, J_{MX}=10.00), 4.68 (dd, 1H, HA, J_{AM}=12.61, J_{AX}=5.54), 6.54 (s, 1H, N$\underline{H}$), 6.94–7.42 (m, 9H, Ar$\underline{H}$). **VIId** (72%) m.p. 121–123°C (Found: C, 43.12; H, 3.00; N, 6.80. $C_{15}H_{12}Cl_2N_2O_4S_2$ requires C, 42.96; H, 2.88; N, 6.86%). ν_{max} (KBr)/cm^{-1} 1360, 1145 (SO_2), 1575 (C=N), 3380 (NH). δ_H (200 MHz; $CDCl_3$) 3.60 (dd, 1H, H_X), 3.92 (dd, 1H, H_M, J_{MX}=9.99), 4.85 (dd, 1H, H_A, J_{AM}=12.61, J_{AX}=5.55), 6.54 (s, 1H, N$\underline{H}$), 6.98–7.37 (m, 8H, Ar$\underline{H}$), **VIIe** (84%) m.p. 137–139°C (Found: C, 48.00;

H, 3.87; N, 7.00. $C_{16}H_{15}ClN_2O_4S_2$ requires C, 48.17; H, 3.79; N, 7.02%). ν_{max} (KBr)/cm^{-1} 1365, 1150 (SO_2), 1570 (C=N), 3365 (NH).

General Procedure for the Preparation of 3-aroylpyrazole (VIII) / 3/4-arylsulfonyl pyrazole (IX/X)

To 5.0 mmol of **I/IV** in 20 ml of dichloromethane, 20 ml of 0.5 M ethereal diazomethane and a catalytic amount of triethylamine was added at 0°C. After standing overnight at the same temperature, the solvent was removed with a rotary evaporator. The resulting gummy product, in the case of **I** when passed through a column of silica gel (60–120 mesh, ether-hexane 2:3) gave **VIII.** However with **IV** the products **IX** and **X** were separated by column chromatography to get analytically pure **IX / X. VIIIa,b,c**(78, 75, 82%) m.p.193–195°C (Found: C, 69.89; H, 4.80; N, 16.22. $C_{10}H_8N_2O$ requires C, 69.75; H, 4.68; N, 16.27%). ν_{max} (KBr)/cm^{-1} 1560 (C=N), 1620 (CO), 3340 (NH). δ_H (200 MHz; $CDCl_3$) 6.45 (s, 1H, N$\underline{H}$), 6.85 (d, 1H, C_5-$\underline{H}$), 7.98 (d, 1H, C_4-$\underline{H}$), 6.92–7.40 (m, 5H, Ar$\underline{H}$). **VIIId,e** (79, 76%) m.p. 165–167°C (Found: C, 58.00; H, 3.38; N, 13.58. $C_{10}H_7ClN_2O$ requires C, 58.12; H, 3.41; N, 13.55%). ν_{max} (KBr)/cm^{-1} 1570 (C=N), 1625 (CO), 3350 (NH). δ_H (200 MHz; $CDCl_3$) 6.46 (s, 1H, N$\underline{H}$), 6.82 (d, 1H, C_5-$\underline{H}$), 8.02 (dd, 1H, C_4-$\underline{H}$), 6.96–7.39 (m, 4H, Ar$\underline{H}$). **IXa,b,c** (42, 58, 56%) m.p. 172–174°C (Found: C, 52.08; H, 3.90; N, 13.50. $C_9H_8N_2O_2S$ requires C, 51.91; H, 3.87; N, 13.45%). ν_{max} (KBr)/cm^{-1} 1350, 1140 (SO_2), 1570 (C=N), 3335 (NH). δ_H (200 MHz; $CDCl_3$) 6.38 (s, 1H, N$\underline{H}$), 6.78 (d, 1H, C_5-$\underline{H}$), 8.02 (d, 1H, C_4-$\underline{H}$), 7.00–7.39 (m, 5H, Ar$\underline{H}$). **IXd,e** (53,40%) m.p. 181–183°C (Found: C, 44.76; H, 3.12; N, 11.66, $C_9H_7ClN_2OS$ requires C, 44.54; H, 2.99; N, 11.54%). ν_{max} (KBr)/cm^{-1} 1360, 1135 (SO_2), 1575 (C=N), 3330 (NH). δ_H (200 MHz; $CDCl_3$) 6.42 (s, 1H, N$\underline{H}$), 6.84 (d, 1H, C_5-$\underline{H}$), 8.05 (d, 1H, C_4-$\underline{H}$), 6.96–7.28 (m, 4H, Ar$\underline{H}$). **Xa** (55%) m.p. 161–163°C (Found: C, 52.08; H, 3.90; N, 13.50. $C_9H_8N_2O_2S$ requires C, 51.91; H, 3.87; N, 13.45%). ν_{max} (KBr)/cm^{-}1340, 1160 (SO_2), 1560 (CN), 3335 (NH). δ_H (200 MHz; $CDCl_3$) 6.39 (s, 1H, N$\underline{H}$), 6.87 (s, 1H, C_5-$\underline{H}$), 7.52 (s, 1H, C_3-$\underline{H}$), 7.01–7.39 (m, 5H, Ar$\underline{H}$). **Xb,d** (40, 43%) m.p. 155–156°C (Found: C, 44.76; H, 3.12; N, 11.66. $C_9H_7ClN_2O_2S$ requires C, 44.54; H, 2.99; N, 11.54%). ν_{max} (KBr)/cm^{-1} 1350, 1150 (SO_2), 1575 (C=N), 3340 (NH). δ_H (200 MHz; $CDCl_3$) 6.42 (s, 1H, N$\underline{H}$), 6.91 (s, 1H, C_5-$\underline{H}$), 7.61 (s, 1H, C_3-$\underline{H}$), 7.00–7.32 (m, 4H, Ar$\underline{H}$). **Xc,e** (41, 58%) m.p. 167–168°C (Found: C, 54.11; H, 4.48; N, 12.69.

$C_{10}H_{10}N_2O_2S$ requires C, 54.04; H, 4.53; N, 12.60%). ν_{max}(KBr)/cm^{-1} 1355, 1145 (SO_2), 1570 (C=N), 3335 (NH).

General Procedure for the dehydrogenation of III/VII (VIII, IX, X)

A solution of 5.0 mmol of **III/VII** and 5.2 mmol of chloranil in 10 ml of xylene was refluxed for 24–32 h. It was washed with 5% NaOH solution. The organic layer was separated and repeatedly washed with water, dried and the solvent was removed with a rotary evaporator. The product formed in the case of **III** was purified by column chromatography. In **VII** the two products **IX** and **X** were separated and purified by column chromatography.

General Procedure for the pyrolysis of III/VII (XI/XII)

A solution of 1.0 mmol of **III/VII** and 10 ml of 1,2-ethanediol was heated at about 200–230°C for 30–45 min. under anhydrous conditions. The contents of the flask were diluted with water and stirred until a solid separated. The crude product **XI/XII** was recrystallized from 2-propanol. **XIa** (43%) m.p. 152–153°C (Found: C, 67.25; H, 4.90. $C_{16}H_{14}O_3S$ requires C, 67.11; H, 4.92%). ν_{max} (KBr)/cm^{-1} 1020 (ring deformation mode), 1330, 1120 (SO_2), 1630 (CO). δ_H (200 MHz; $CDCl_3$) 1.39 (ddd, 1H, H_N), 1.84 (ddd, 1H, H_M), 2.65 (ddd, 1H, H_B), 2.78 (ddd, 1H, HA), 6.98–7.42 (m, 10H, Ar<u>H</u>), J_{AB}=5.74, J_{AM}=8.55, J_{AN}=6.58, J_{BM}=5.55, J_{BN}=10.12, J_{MN}=4.66. **XIb** (58%) m.p. 160–161°C (Found: C, 60.10; H, 4.13. $C_{16}H_{13}ClO_3S$ requires C, 59.90; H, 4.08%). ν_{max} (KBr)/cm^{-1} 1025 (ring deformation mode), 1335, 1130 (SO_2), 1650 (CO). **XIc** (60%) m.p. 177–178°C (Found: C, 68.00; H, 5.42. $C_{17}H_{16}O_3S$ requires C, 67.97; H, 5.36%). ν_{max}(KBr)/cm^{-1} 1020 (ring deformation mode), 1330, 1135 (SO_2), 1640 (CO). δ_H (200 MHz; $CDCl_3$) 1.45 (ddd, 1H, H_N), 1.89 (ddd, 1H, HM), 2.58 (ddd, 1H, H_B), 2.75 (ddd, 1H, H_A), 2.21 (s, 3H, Ar C<u>H</u>$_3$), 6.85–7.38 (m, 9H, Ar<u>H</u>), J_{AB}=5.72, J_{AM}=8.59, J_{AN}=6.59, J_{BM}=5.57, J_{BN}=10.14, J_{MN}=4.64. **XId** (64%) m.p. 147–148°C (Found: C, 54.00; H, 3.47. $C_{16}H_{12}Cl_2O_3S$ requires C, 54.09; H, 3.40%). ν_{max} (KBr)/cm^{-1} 1030 (ring deformation mode), 1340, 1130 (SO_2), 1655 (CO). **XIe** (68%) m.p. 183–184°C (Found: C, 61.06; H, 4.61. $C_{17}H_{15}ClO_3S$ requires C, 60.98; H, 4.51%). ν_{max} (KBr)/cm^{-1} 1025 (ring deformation mode), 1335, 1140 (SO_2), 1650 (CO). δ_H (200 MHz; $CDCl_3$) 1.44 (ddd, 1H, H_N), 1.89 (ddd, 1H, H_M), 2.58 (ddd, 1H, H_B), 2.75 (ddd, 1H, H_A), 2.18 (s, 3H, Ar C<u>H</u>$_3$), 6.98–7.45 (m, 8H, Ar<u>H</u>), J_{AB}=5.72, J_{AM}=8.59, J_{AX}=6.59, J_{BM}=5.57, J_{BN}=10.14, J_{MN}=4.64. **XIIa** (62%) m.p. 150–151°C (Found: C, 56.00; H, 4.40. $C_{15}H_{14}O_4S_2$ requires C, 55.88; H, 4.37%). ν_{max} (KBr)/cm^{-1} 1020 (ring deformation mode), 1330, 1120 (SO_2). **XIIb** (66%) m.p. 167–168°C (Found: C, 50.42; H, 3.73. $C_{15}H_{13}ClO_4S_2$ requires C, 50.48; H, 3.67%). ν_{max}(KBr/cm^{-1}) 1025 (ring deformation mode), 1330, 1145 (SO_2). **XIIc** (67%) m.p. 194–195°C (Found: C, 57.00; H, 4.70. $C_{16}H_{16}O_4S_2$ requires C, 57.12; H, 4.79%). ν_{max}(KBr)/cm^{-1} 1020 (ring deformation mode), 1340, 1130 (SO_2). δ_H (200 MHz; $CDCl_3$) 2.24 (s, 3H, ArC<u>H</u>$_3$), 2.85–2.89 (m, 2H, C<u>H</u>$_2$), 3.50–3.55 (m, 2H, 2C<u>H</u>), 6.95–7.29 (m, 9H, Ar<u>H</u>). **XIId** (65%) m.p. 153–154°C (Found: C, 46.22; H, 3.24. $C_{15}H_{12}Cl_2O_4S_2$ requires C, 46.04; H, 3.09%). ν_{max} (KBr)/cm^{-1} 1030 (ring deformation mode), 1320, 1140 (SO_2). δ_H (200 MHz; $CDCl_3$) 2.94–3.00 (m, 2H, C<u>H</u>$_2$), 3.53–3.58 (m, 2H, 2C<u>H</u>), 7.01–7.25 (m, 8H, Ar<u>H</u>). **XIIe** (74%) m.p. 196–198°C (Found: C, 51.97; H, 4.14. $C_{16}H_{15}ClO_4S_2$ requires C, 51.81; H, 4.07%). ν_{max} (KBr)/cm^{-1} 1025 (ring deformation mode), 1330, 1145 (SO_2). δ_H (200 MHz; $CDCl_3$), 2.87 – 2.92 (m, 2H, C<u>H</u>$_2$), 3.52 – 3.55 (m, 2H, 2C<u>H</u>), 6.99 – 7.24 (m, 8H, Ar<u>H</u>).

General Procedure for the nitrosation of III/VII (XIIIa/XIVa)

A well cooled solution of 1.0 mmol of **III/VII** in 8 ml of 2N hydrochloric acid was treated with a cold saturated solution of sodium nitrite (10 ml) and kept in an ice-bath. The solid separated was collected, washed with water, dried and recrystallized from ethanol. **XIIIa** (82%) m.p. 115–116°C. **XIVa** (80%) m.p. 111–112°C.

General Procedure for the acylation of III/VII (XIIIb-d/XIVb-d)

A solution of 1.0 mmol of **III/VII** in 5 ml of pyridine and 1.0 mmol of benzoyl (or) benzenesulfonyl chloride (for acetylation 1.0 mmol of **III/VII** was taken in a mixture containing 5 ml of glacial acetic acid and 2 ml of acetic anhydride) was refluxed for 2–3 h. The contents were poured onto crushed ice containing conc. hydrochloric acid. The products obtained are recrystallized from alcohol. **XIIIb** (80%) m.p. 127–128°C. **XIIIc** (86%) m.p. 121–122°C. **XIIId** (78%) m.p. 135–136°C. **XIVb** (85%) m.p. 115–116°C. **XIVc** (79%) m.p. 124–125°C. **XIVd** (72%) m.p. 119–120°C.

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