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# SYNTHESIS OF PYRROLYL AND PYRAZOLYL SULFONAMIDES

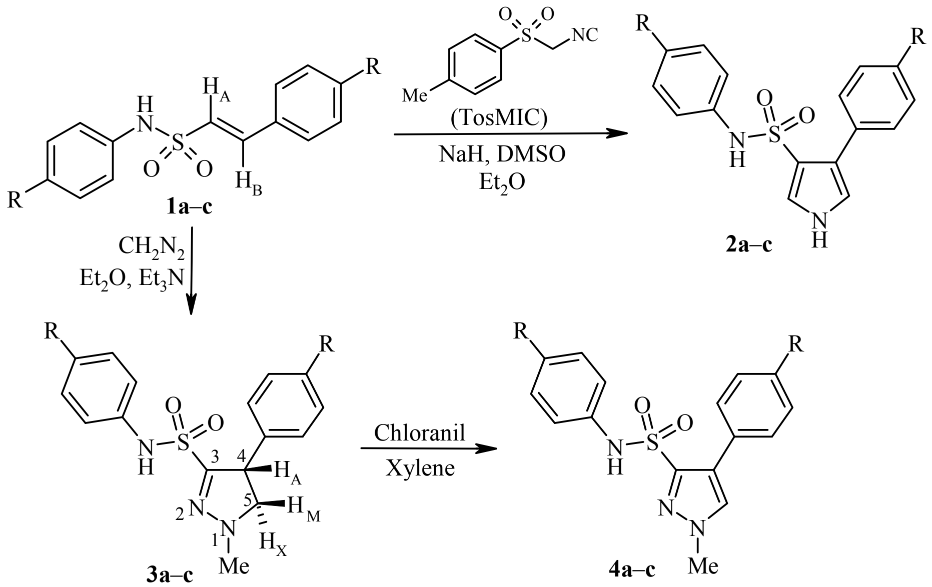
A new class of pyrrolyl and pyrazolyl sulfonamides was prepared from styrene-ω-sulfonanilides by treatment with tosylmethyl isocyanide and diazomethane, respectively.

**Keywords:** diazomethane, pyrazolylsulfonamide, pyrrolylsulfonamide, styrene-ω-sulfonanilides, tosylmethyl isocyanide.

Scientific efforts have continuously been directed towards the design and synthesis of five-membered heterocycles because of their utility as pharmacological agents. Netropsin and Distamycin are pyrrole polyamides and are naturally occurring anticancer antibiotics [1]. Multistep synthetic routes for 3,4-disubstituted pyrroles have been reported either by coupling of imines and nitroalkanes or using Friedel–Craft's acylation with an electron withdrawing group on pyrrole nitrogen or 3,4-silylated precursors [2]. Pyrroles have also been prepared from Michael acceptors and tosylmethyl isocyanide (TosMIC) [3, 4]. Several pyrazole derivatives received increased attention due to their biological activities as potential HIV-1 inhibitors [5], insecticides [6], fungicides [6], antiviral [7], anti-inflammatory [8], antiobesity [9] and anticancer agents [10]. Amongst different known methods for the synthesis of pyrazoles, Huisgen's 1,3-dipolar cycloaddition is a versatile one [11]. Recent syntheses of pyrazoles *via* 1,3-dipolar cycloaddition includes reaction of nitrile imines and alkynes [12] or enamines [13], hydrazones and nitroolefins [14], diazocompounds and alkynes [15], and azomethine imines and alkynes [16]. We have exploited various activated olefins for the synthesis of a variety of mono- and bis-heterocycles [17, 18]. However, there are no reports to our knowledge about the use of styrenesulfonamides for the development of five-membered heterocycles.

The present communication deals with the synthesis of pyrrolyl and pyrazolyl sulfonamides from styrene-ω-sulfonanilides **1a**–**c**. The compounds **1a**–**c** were prepared by the Knoevenagel's condensation of arylaminosulfonylacetic acids with arylaldehydes. The arylaminosulfonylacetic acids were obtained by the well-known chain of reactions from substituted anilines [19].

The olefin group present in compounds **1a**–**c** was exploited to develop pyrrole and pyrazoline rings. Treatment of compounds **1a**–**c** with TosMIC gave 4-aryl-3-arylaminosulfonylpyrroles **2a**–**c**. The $^1$H NMR spectrum of compound **2a** showed two singlets at 6.56 and 7.17 ppm due to H-2 and H-5 protons of pyrrole ring in addition to two broad singlets at 8.41 and 10.45 ppm due to $SO_2$NH and NH fragments. The latter signals disappeared by deuteration. Similarly 1,3-dipolar cycloaddition of diazomethane to compounds **1a**–**c** at a temperature of about –20°C produced 4-aryl-3-arylaminosulfonyl-1-methylpyrazolines **3a**–**c**. It appears that *N*-methylation also took place during the course of cyclization.



**a** R = H, **b** R = Me, **c** R = Cl

The [1]H NMR spectrum of compound **3a** showed AMX splitting pattern for methine and methylene protons of pyrazoline ring. The three double doublets observed at 4.22, 3.94 and 3.55 ppm were assigned to pyrazoline ring protons $H_A$, $H_M$ and $H_X$, respectively. The coupling constants indicated that $H_A$ and $H_M$ are in *cis*, $H_A$ and $H_X$ – *trans*, and $H_M$ and $H_X$ – in geminal position to each other. A sharp singlet was observed at 3.14 ppm due to $NCH_3$ group. Apart from these, a broad singlet was observed at 8.37 ppm due NH which disappeared on deuteration. Aromatization of compounds **3a–c** with chloranil in xylene resulted in 4-aryl-3-arylaminosulfonyl-1-methylpyrazoles **4a–c**. The absence of AMX splitting pattern confirmed the formation of compounds **4a–c**. The $^1H$ NMR spectrum of compound **4a** displayed two sharp singlets due to $NCH_3$ group and H-5 proton (overlapping with multiplet signal of phenyl protons), and a broad singlet due to NH proton. The signal due to NH disappeared by deuteration. The structures of the compounds were further established by IR and $^{13}C$ NMR spectra.

Thus, a simple substrate, styrene-ω-sulfonanilide, was exploited to obtain a new sulfonamide linked pyrroles and pyrazoles adopting 1,3-dipolar cycloaddition methodology.

## EXPERIMENTAL

The IR spectra were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer in KBr pellets. The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Spectrospin instrument (400 and 100 MHz, respectively) in DMSO-$d_6$ using TMS as internal standard. The elemental microanalyses were performed on a Perkin Elmer 240C Elemental Analyzer. Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by TLC (silica gel H, BDH, eluent EtOAc–hexane, 1:3). The starting arylaminosulfonylacetic acids were prepared by the literature procedure [19].

**Styrene-ω-sulfonanilides 1a–c** (General Method). A mixture of arylaldehyde (1 mmol), pyridine (4 ml), $AcONH_4$ (1.00 g, 13 mmol), arylaminosulfonylacetic acid (0.21 g, 1 mmol), and toluene (25 ml) were refluxed for 20–24 h with azeotropic removal of water. The solution was cooled and washed successively with dilute HCl, dilute $Na_2SO_3$, and brine. Then it was extracted with 10% KOH. The potassium salt of styrene sulfonamide was separated as oil with the aqueous phase. The two phase aqueous extract was washed with ether and acidified with HCl. Then, it was extracted with ether. Removal of the solvent under vacuum furnished a solid which on recrystallization from cyclohexane gave compounds **1a**–**c**.

***(E)*-*N*,2-Diphenylethenesulfonamide (1a)**. Yield 0.20 g (77%). White solid. Mp 108–112°C (mp 113°C [19]). IR spectrum, ν, $cm^{-1}$: 3332 (NH), 1632 (C=C), 1317, 1138 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.45 (1H, br. s, NH); 8.04 (1H, d, *J* = 14.7, $H_A$); 7.84 (1H, d, *J* = 14.7, $H_B$); 7.22–7.38 (10H, m, H Ph). $^{13}C$ NMR spectrum, δ, ppm: 145.4 ($CH_A$); 131.3 ($CH_B$); 139.3, 136.1, 134.2, 133.8, 131.2, 126.7, 125.6, 124.3 (C Ph). Found, %: C 64.75; H 5.01; N 5.48. $C_{14}H_{13}NO_2S$. Calculated, %: C 64.84; H 5.05; N 5.40.

***(E)*-*N*,2-Bis(4-methylphenyl)ethenesulfonamide (1b)**. Yield 0.23 g (83%). White solid. Mp 124–126°C. IR spectrum, ν, $cm^{-1}$: 3348 (NH), 1625 (C=C), 1320, 1143 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.48 (1H, br. s, NH); 8.02 (1H, d, *J* = 14.6, $H_A$); 7.87 (1H, d, *J* = 14.6, $H_B$); 7.15–7.38 (8H, m, H Ar); 2.39 (3H, s, $CH_3$), 2.37 (3H, s, $CH_3$). $^{13}C$ NMR spectrum, δ, ppm: 144.6 ($CH_A$); 131.5 ($CH_B$); 137.2, 136.8, 133.7, 132.5, 130.9, 127.4, 124.8, 124.2 (C Ar); 23.7 ($CH_3$); 23.5 ($CH_3$). Found, %: C 66.93; H 5.87; N 4.82. $C_{16}H_{17}NO_2S$. Calculated, %: C 66.87; H 5.96; N 4.87.

***(E)*-*N*,2-Bis(4-chlorophenyl)ethenesulfonamide (1c)**. Yield 0.25 g (77%). White solid. Mp 116–118°C. IR spectrum, ν, $cm^{-1}$: 3341 (NH), 1628 (C=C), 1323, 1146 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.42 (1H, br. s, NH); 8.08 (1H, d, *J* = 14.8, $H_A$); 7.89 (1H, d, *J* = 14.8, $H_B$); 7.25–7.39 (8H, m, H Ar). $^{13}C$ NMR spectrum, δ, ppm: 146.7 ($CH_A$); 131.8 ($CH_B$); 138.4, 136.2, 131.8, 131.4, 129.7, 129.5, 126.5, 126.1, 124.5 (C Ar). Found, %: C 51.28; H 3.35; N 4.32. $C_{14}H_{11}Cl_2NO_2S$. Calculated, %: C 51.23; H 3.38; N 4.27.

**4-Aryl-3-arylaminosulfonylpyrroles 2a–c** (General Method). In a 100 ml two-necked round-bottomed flask fitted with a calcium chloride guard-tube, a septum and equipped with a magnetic stirrer, NaH (0.06 g, 2.5 mmol) in abs. $Et_2O$ (8 ml) was stirred at rt for 20 min. To this, a mixture of TosMIC (0.97 g, 5.0 mmol) and compound **1a**–**c** (1.29 g, 5.0 mmol) in DMSO (8 ml) and abs. $Et_2O$ (4 ml) was added dropwise *via* a syringe. The stirring was continued for another 18–20 h and diluted with $H_2O$. It was extracted with $Et_2O$ and dried over anhydrous $Na_2SO_4$. Removal of the solvent *in vacuo* gave crude product which was purified by column chromatography (eluent EtOAc–hexane, 1:3).

**4-Phenyl-3-phenylaminosulfonylpyrrole (2a)**. Yield 1.02 g (69%). White solid. Mp 125–127°C. IR spectrum, ν, $cm^{-1}$: 3235 (NH), 1621 (C=C), 1335, 1147 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 10.45 (1H, br. s, NH); 8.41 (1H, br. s, $SO_2NH$); 7.22–7.82 (10H, m, H Ph); 7.17 (1H, s, H-5); 6.56 (1H, s, H-2). $^{13}C$ NMR spectrum, δ, ppm: 137.8, 135.9, 131.2, 130.8, 128.3, 126.8, 126.2, 122.8 (C Ph); 120.5 (C-5); 115.7 (C-2); 105.8 (C-4); 104.5 (C-3). Found, %: C 64.53; H 4.67; N 9.32. $C_{16}H_{14}N_2O_2S$. Calculated, %: C 64.41; H 4.73; N 9.39.

**4-(4-Methylphenyl)-3-(4-methylphenyl)aminosulfonylpyrrole (2b)**. Yield 1.06 g (65%). White solid. Mp 146–148°C. IR spectrum, ν, $cm^{-1}$: 3238 (NH), 1625 (C=C), 1339, 1132 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 10.44 (1H, br. s, NH); 8.43 (1H, br. s, $SO_2NH$); 7.18–7.86 (8H, m, H Ar); 7.13 (1H, s, H-2); 6.68 (1H, s, H-5); 2.34 (3H, s, $CH_3$); 2.32 (3H, s, $CH_3$). $^{13}C$ NMR spectrum, δ, ppm: 138.1, 136.5, 131.8, 130.5, 128.8, 127.4, 125.9, 123.6 (C Ar); 119.8 (C-5); 114.2 (C-2); 105.9 (C-4); 104.7 (C-3); 23.4 ($CH_3$); 23.1 ($CH_3$). Found, %: C 66.14; H 5.61; N 8.66. $C_{18}H_{18}N_2O_2S$. Calculated, %: C 66.23; H 5.56; N 8.58.

**4-(4-Chlorophenyl)-3-(4-chlorophenyl)aminosulfonylpyrrole (2c)**. Yield 1.24 g (68%). White solid. Mp 163–165°C. IR spectrum, ν, $cm^{-1}$: 3343 (NH), 1618 (C=C), 1337, 1143 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 10.47 (1H, br. s, NH); 8.45 (1H, br. s, $SO_2NH$); 7.25–7.91 (8H, m, H Ar); 7.23 (1H, s, H-5); 6.54 (1H, s, H-2). $^{13}C$ NMR spectrum, δ, ppm: 137.5, 136.8, 130.1, 129.7, 128.9, 128.8, 122.2, 121.9 (C Ar); 117.5 (C-5); 113.2 (C-2); 106.4 (C-4); 102.1 (C-3). Found, %: C 52.45; H 3.32; N 7.71. $C_{16}H_{12}Cl_2N_2O_2S$. Calculated, %: C 52.33; H 3.29; N 7.63.

**4-Aryl-3-arylaminosulfonyl-1-methylpyrazolines 3a–c** (General Method). To a cooled solution of compound **1a**–**c** (0.64 g, 2.5 mmol) in $CH_2Cl_2$ (10 ml), and 0.4M $Et_2O$ solution of $CH_2N_2$ (20 ml) and $Et_3N$ (0.06 g, 0.6 mmol) were added. The reaction mixture was kept at –20 to –15°C temperature for 40–48 h. The solvent was removed under reduced pressure. The resultant solid was purified by column chromatography (eluent EtOAc–hexane, 1:3).

**1-Methyl-4-phenyl-3-phenylaminosulfonylpyrazoline (3a)**. Yield 0.55 g (71%). White solid. Mp 136–138°C. IR spectrum, ν, $cm^{-1}$: 3327 (NH), 1589 (C=N), 1335, 1141 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.37 (1H, br. s, NH); 7.02–7.33 (10H, m, H Ph); 4.22 (1H, dd, $J_{AM}$ = 12.0, $J_{AX}$ = 6.9, $H_A$); 3.94 (1H, dd, $J_{AM}$ = 12.0, $J_{MX}$ = 10.9, $H_M$); 3.55 (1H, dd, $J_{AX}$ = 6.9, $J_{MX}$ = 10.9, $H_X$); 3.14 (3H, s, $NCH_3$). $^{13}C$ NMR spectrum, δ, ppm: 137.5, 136.8, 130.1, 129.7, 128.9, 128.8, 122.2, 121.9 (C Ph); 117.5 (C-5); 113.2 (C-2); 106.4 (C-4); 102.1 (C-3). Found, %: C 61.04; H 5.43; N 13.20. $C_{16}H_{17}N_3O_2S$. Calculated, %: C 60.93; H 5.43; N 13.32.

**1-Methyl-4-(4-methylphenyl)-3-(4-methylphenyl)aminosulfonylpyrazoline (3b)**. Yield 0.61 g (72%). White solid. Mp 152–154°C. IR spectrum, ν, $cm^{-1}$: 3342 (NH), 1594 (C=N), 1340, 1138 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.45 (1H, br. s, NH); 7.13–7.52 (8H, m, H Ar); 4.30 (1H, dd, $J_{AM}$ = 12.3, $J_{AX}$ = 6.7, $H_A$); 3.95 (1H, dd, $J_{AM}$ = 12.3, $J_{MX}$ = 10.7, $H_M$); 3.52 (1H, dd, $J_{AX}$ = 6.7, $J_{MX}$ = 10.7, $H_X$); 3.11 (3H, s, $NCH_3$); 2.37 (3H, s, $ArC\underline{H}_3$); 2.35 (3H, s, $ArC\underline{H}_3$). $^{13}C$ NMR spectrum, δ, ppm: 148.7 (C-3); 139.5, 136.7, 132.8, 131.6, 130.2, 128.8, 126.4, 123.7 (C Ar); 56.5 (C-5); 51.2 (C-4); 42.3 ($NCH_3$); 23.7 ($Ar\underline{C}H_3$); 23.5 ($Ar\underline{C}H_3$). Found, %: C 63.06; H 6.11; N 12.33. $C_{18}H_{21}N_3O_2S$. Calculated, %: C 62.95; H 6.16; N 12.23.

**4-(4-Chlorophenyl)-3-(4-chlorophenyl)aminosulfonyl-1-methylpyrazoline (3c).** Yield 0.72 g (75%). White solid. Mp 187–189°C. IR spctrum, ν, $cm^{-1}$: 3344 (NH), 1606 (C=N), 1336, 1144 ($SO_2$). $^1H$ NMR spectrum, δ, ppm (*J*, Hz): 8.41 (1H, br. s, NH); 7.10–7.45 (8H, m, H Ar); 4.28 (1H, dd, $J_{AM}$ = 12.4, $J_{AX}$ = 6.8, $H_A$); 3.97 (1H, dd, $J_{AM}$ = 12.4, $J_{MX}$ = 11.0, $H_M$); 3.52 (1H, dd, $J_{AX}$ = 6.8, $J_{MX}$ = 11.0, $H_X$); 3.10 (3H, s, $NCH_3$). $^{13}C$ NMR spectrum, δ, ppm: 146.5 (C-3); 140.5, 137.6, 132.4, 130.2, 129.2, 128.8, 127.9, 122.2 (C Ar); 59.3 (C-5); 51.9 (C-4); 42.9 ($NCH_3$). Found, %: C 49.92; H 3.97; N 11.05. $C_{16}H_{15}Cl_2N_3O_2S$. Calculated, %: C 50.01; H 3.93; N 10.93.

**4-Aryl-3-arylaminosulfonyl-1-methylpyrazoles 4a–c** (General Method). A solution of compound **3a**–**c** (0.32 g, 1 mmol) and chloranil (0.25 g, 1 mmol) in xylene (10 ml) was refluxed for 24–32 h. Then the reaction mixture was treated with a 5% NaOH solution. The organic layer was separated and repeatedly washed with water. It was dried over anhydrous $Na_2SO_4$, and the solvent was removed on a rotary evaporator. The resultant solid was purified by recrystallization from 2-PrOH.

**1-Methyl-4-phenyl-3-phenylaminosulfonylpyrazole (4a)**. Yield 0.20 g (65%). White solid. Mp 155–157°C. IR spectrum, ν, $cm^{-1}$: 3340 (NH), 1623 (C=C), 1583 (C=N), 1333, 1140 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 8.35 (1H, br. s, NH); 6.98–7.35 (11H, m, H-5, H Ph); 3.27 (3H, s, $NCH_3$). $^{13}C$ NMR spectrum, δ, ppm: 149.5 (C-3); 138.6 (C-5); 137.4 (C-4); 138.2, 136.8, 132.5, 131.8, 129.3, 128.2, 126.4, 125.8 (C Ph); 42.8 ($NCH_3$). Found, %: C 61.45; H 4.87; N 13.52. $C_{16}H_{15}N_3O_2S$. Calculated, %: C 61.32; H 4.82; N 13.41.

**1-Methyl-4-(4-methylphenyl)-3-(4-methylphenyl)aminosulfonylpyrazole (4b)**. Yield 0.22 g (67%). White solid. Mp 174–176°C. IR spectrum, ν, $cm^{-1}$: 3340 (NH), 1623 (C=C), 1583 (C=N), 1333, 1140 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 8.32 (1H, br. s, NH); 6.92–7.32 (9H, m, H-5, H Ar); 3.24 (3H, s, $NCH_3$); 2.35 (3H, s, $ArC\underline{H}_3$); 2.32 (3H, s, $ArC\underline{H}_3$). $^{13}C$ NMR spectrum, δ, ppm: 149.8 (C-3); 138.1 (C-5); 136.8 (C-4); 137.3, 135.6, 132.2, 131.5, 129.8, 129.1, 128.3, 125.4 (C Ar); 42.5 ($NCH_3$); 23.9 ($Ar\underline{C}H_3$), 23.7 ($Ar\underline{C}H_3$). Found, %: C 63.25; H 5.66; N 12.40. $C_{18}H_{19}N_3O_2S$. Calculated, %: C 63.32; H 5.61; N 12.31.

**4-(4-Chlorophenyl)-3-(4-chlorophenyl)aminosulfonyl-1-methylpyrazole (4c).** Yield 0.25 g (68 %). White solid. Mp 201–203°C. IR spectrum, ν, $cm^{-1}$: 3347 (NH), 1625 (C=C), 1603 (C=N), 1337, 1145 ($SO_2$). $^1H$ NMR spectrum, δ, ppm: 8.38 (1H, br. s, NH); 7.04–

7.39 (9H, m, H-5, H Ar); 3.24 (3H, s, $NCH_3$). $^{13}C$ NMR spectrum, δ, ppm: 148.7 (C-3); 139.6 (C-5); 138.8 (C-4); 138.7, 136.2, 132.8, 131.3, 129.5, 128.4, 127.5, 125.6 (C Ar); 43.0 ($NCH_3$). Found, %: C 50.34; H 3.38; N 11.06. $C_{16}H_{13}Cl_2N_3O_2S$. Calculated, %: C 50.27; H 3.43; N 10.99.

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