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Novel 2-pyrazolines were obtained by the cycloaddition of diazomethane to bis(arylsulfonylethenyl)-sulfones (**3**) and 1-arylsulfonyl-2-styrylsulfonylethenes (**7**). Dehydrogenation of 2-pyrazolines with chloranil gave pyrazoles.

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Introduction.

α,β -Unsaturated sulfones are valuable intermediates in a variety of synthetic transformations and useful as building blocks in the synthesis of biologically active heterocycles [1]. One such class of compounds includes pyrazole and its derivatives, which continue to attract considerable attention in various fields because of their wide range of biological and physical applications. In fact celecoxib which is a pyrazole derivative is now widely used in the market as a potential anti-inflammatory drug [2]. Though there are different methods for their syntheses, the 1,3-dipolar cycloaddition of diazomethane to an olefin is a well known process.

Adopting this methodology, herein we report our results in the reaction of sulfonyl activated bis olefinic systems with diazomethane. In fact the addition of diazomethane to activated olefins results initially in 1-pyrazolines which tautomerized to 2-pyrazolines as a consequence of the migration of more acidic proton [3].

When bis (2-arylsulfonylethenyl)-[1,1']-sulfone (**3**) was subjected to cycloaddition with diazomethane, instead of the expected bis pyrazolines by 2+3 cycloaddition of latter across the two double bonds, a mixture of mono- and bis-

Scheme 1

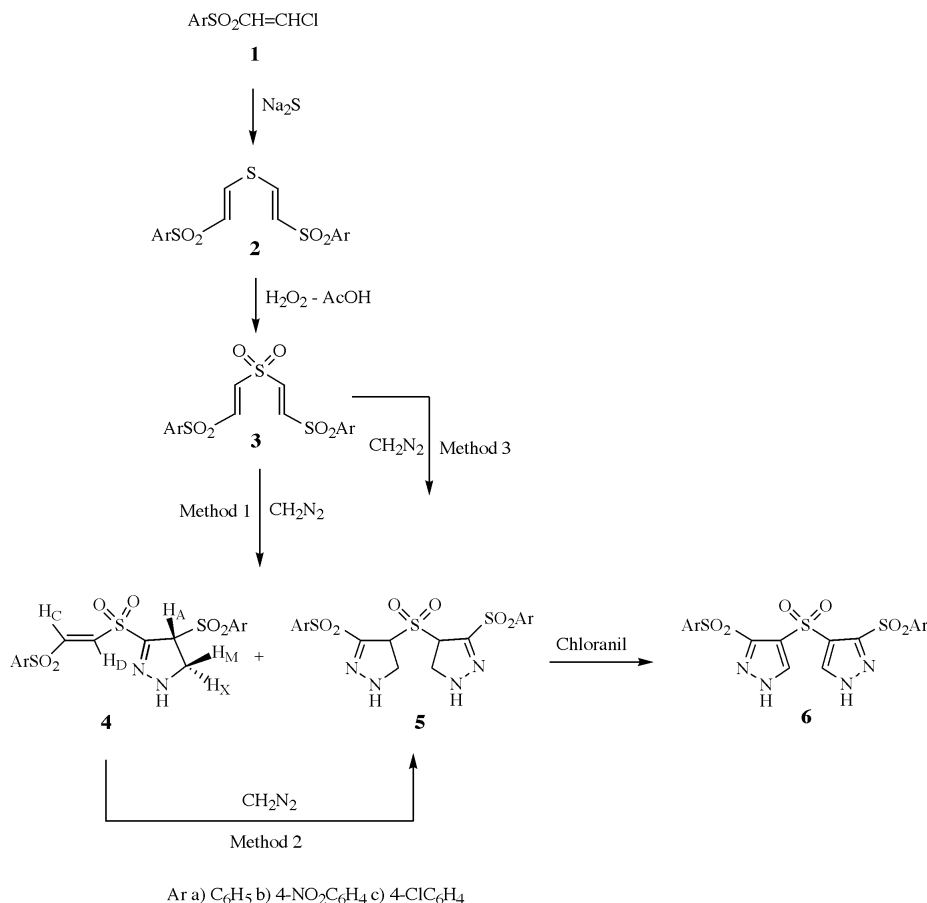


Table 1
Physical Properties for Compounds 2-11

Compd.	mp (°C)	Yield (%)	Mol formula (Molecular weight)	Calcd. (Found) %		
				C	H	N
2a	164-166	70	-	-	-	-
2b	192-194	90	-	-	-	-
2c	178-180	74	-	-	-	-
3a	204-206	70	-	-	-	-
3b	188-190	68	-	-	-	-
3c	220-222	74	-	-	-	-
4a	146-148	57	C ₁₇ H ₁₆ N ₂ O ₆ S ₃ (440.53)	46.35 (46.51)	3.66 (3.54)	6.36 (6.42)
4b	138-140	59	C ₁₇ H ₁₄ N ₄ O ₁₀ S ₃ (530.52)	38.49 (38.38)	2.66 (2.73)	10.56 (10.48)
4c	152-154	55	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₆ S ₃ (509.41)	40.08 (40.19)	2.77 (2.63)	5.50 (5.38)
5a	161-163	26 63* 74**	C ₁₈ H ₁₈ N ₄ O ₆ S ₃ (482.56)	44.80 (44.62)	3.76 (3.64)	11.61 (11.74)
5b	168-170	25 61* 70**	C ₁₈ H ₁₆ N ₆ O ₁₀ S ₃ (572.56)	37.76 (37.88)	2.82 (2.74)	14.68 (14.79)
5c	173-175	26 68* 75**	C ₁₈ H ₁₆ Cl ₂ N ₄ O ₆ S ₃ (551.45)	39.20 (39.09)	2.92 (2.83)	10.16 (10.32)
6a	152-154	72	C ₁₈ H ₁₄ N ₄ O ₆ S ₃ (478.53)	45.18 (45.32)	2.95 (2.89)	11.71 (11.84)
6b	144-146	83	C ₁₈ H ₁₂ N ₆ O ₁₀ S ₃ (568.52)	38.03 (38.14)	2.13 (2.21)	14.78 (14.63)
6c	163-165	76	C ₁₈ H ₁₂ Cl ₂ N ₄ O ₆ S ₃ (547.42)	39.49 (39.35)	2.21 (2.16)	10.24 (10.37)
8a	129-131	14	C ₁₇ H ₁₆ N ₂ O ₄ S ₂ (376.46)	54.24 (54.10)	4.28 (4.35)	7.44 (7.34)
8b	142-144	17	C ₁₇ H ₁₅ N ₃ O ₆ S ₂ (421.46)	48.45 (48.32)	3.59 (3.51)	9.97 (10.04)
8c	131-133	16	C ₁₇ H ₁₅ ClN ₂ O ₄ S ₂ (410.90)	49.69 (49.79)	3.68 (3.60)	6.82 (6.73)
9a	143-145	42	C ₁₇ H ₁₆ N ₂ O ₄ S ₂ (376.46)	54.24 (54.12)	4.28 (4.32)	7.44 (7.36)
9b	128-130	40	C ₁₇ H ₁₅ N ₃ O ₆ S ₂ (421.46)	48.45 (48.55)	3.59 (3.53)	9.97 (10.07)
9c	152-154	38	C ₁₇ H ₁₅ ClN ₂ O ₄ S ₂ (410.90)	49.69 (49.50)	3.68 (3.61)	6.82 (6.77)
10a	161-163	28 69* 73**	C ₁₈ H ₁₈ N ₄ O ₄ S ₂ (418.50)	51.66 (51.78)	4.33 (4.21)	13.39 (13.14)
10b	149-151	29 72* 75**	C ₁₈ H ₁₇ N ₅ O ₆ S ₂ (463.49)	46.65 (46.74)	3.70 (3.62)	15.11 (15.24)
10c	156-158	28 76* 79**	C ₁₈ H ₁₇ ClN ₄ O ₄ S ₂ (452.94)	47.73 (47.84)	3.73 (3.69)	12.37 (12.20)
11a	139-141	76	C ₁₈ H ₁₄ N ₄ O ₄ S ₂ (414.46)	52.16 (52.32)	3.40 (3.36)	13.52 (13.67)
11b	123-125	73	C ₁₈ H ₁₃ N ₅ O ₆ S ₂ (459.46)	47.05 (47.17)	2.85 (2.79)	15.24 (15.36)
11c	133-135	76	C ₁₈ H ₁₃ ClN ₄ O ₄ S ₂ (448.91)	48.16 (48.02)	2.92 (3.00)	12.48 (12.63)

* Yield using Method 2; ** yield using Method 3.

pyrazolines were obtained. (Scheme 1 and Table 1). They were separated by column chromatography. The ¹H NMR spectra of the major product showed AMX splitting pattern for pyrazoline ring protons and exhibited three double doublets in the regions 4.96-5.09 (H_A), 4.42-4.49 (H_M), 3.83-3.85 (H_X). The coupling constant values J_{AM} = 12.6, J_{MX} = 10.1 and J_{AX} = 5.5 Hz indicates that H_A, H_M are

cis, H_A, H_X are *trans* and H_M, H_X are *geminal*. Apart from this a doublet was observed at 6.65-6.68 for H_C while H_D merged with aromatic protons and appeared as a multiplet. The coupling constant (14.2 Hz) indicates that they possess *trans* geometry. However, the minor one displayed three double doublets for H_A, H_M and H_X of the two pyrazoline rings in the regions 4.96-5.01, 4.42-4.49 and 3.80-

3.85. Infact, the highly symmetrical nature of this compound is confirmed by integration. All the compounds displayed broad singlet around 10.22-10.30 ppm for NH protons that disappeared on deuteration. Thus they were identified as 2'-arylsulfonylethenyl-3-arylsulfonyl-2-pyrazoliny-[4,1']-sulfone (**4**) (major) and bis (3-arylsulfonyl-2-pyrazoliny)-[4,4']-sulfone (**5**) (minor). Treatment of **4** with one more mole of diazomethane resulted in **5**. The latter was also obtained directly when **3** was treated with excess diazomethane. The reaction of **5** with chloranil in xylene gave bis (3-arylsulfonylpyrazolyl)-[4,4']-sulfone (**6**) [4]. The ^1H NMR spectrum of **6** showed a broad singlet at 10.34 for two NH protons and a multiplet between 6.98-7.92 for aromatic and pyrazolyl ring protons (Table 2). The signals due to NH disappeared on deuteration.

Similarly, when 1-arylsulfonyl-2-styrylsulfonylethene (**7**) was treated with diazomethane, instead of expected bis pyrazolines, a mixture of mono and bis adducts were obtained. They were separated by column chromatography and identified as 3-arylsulfonyl-2-pyrazoliny-4-styrylsulfone (**8**), 2-arylsulfonylethenyl-4'-aryl-2'-pyrazoliny-[1,3']-sulfone (**9**) and 3-arylsulfonyl-2-pyrazoliny-4'-aryl-2'-pyrazoliny-[4,3']-sulfone (**10**) by their ^1H NMR spectra (Scheme 2 and Table 1). The spectrum of **8** showed AMX splitting pattern for pyrazoline ring protons and exhibited double doublets in the regions 4.98-5.04 (H_A), 4.45-4.53 (H_M) and 3.82-3.88 (H_X). The coupling constant values $J_{AM} = 12.6$, $J_{AX} = 5.5$ and $J_{MX} = 10.0$ Hz indicates that H_A , H_M are *cis*, H_A , H_X are *trans* and H_M , H_X are *geminal*. Apart from this a doublet was observed in the region 6.66-6.68 for H_C . Another proton, H_D merged with aromatic protons and appeared as a multiplet. The spectrum of **9** exhibited three double doublets

at 4.62-4.68, 4.10-4.16 and 3.45-3.52 which are due to methine (H_A) and methylene (H_M and H_X) protons of pyrazoline ring as in **8**. Moreover, a doublet was observed at 6.66-6.69, which accounted for H_D . The signal for H_C merged with that of the aromatic protons and appeared as a multiplet. On the other hand **10** displayed six sets of double doublets in the region 4.98-5.04 (H_A), 4.45-4.53 (H_M), 3.82-3.88 (H_X), 4.62-4.68 (H_A'), 4.10-4.16 (H_M') 3.45-3.52 (H_X') which indicated that the two pyrazoline rings are in different environments. All the compounds showed a broad singlet around 10.20-10.32 for NH, which disappeared on deuteration. However treatment of **7** with two fold excess of diazomethane gave only **10**. The latter was also obtained by the treatment of **9** with diazomethane. The authenticity of **10** obtained by different routes was confirmed by TLC and ^1H NMR spectra. Oxidation of **10** with chloranil in xylene gave 3-arylsulfonylpyrazolyl-4-(4'-arylpyrazolyl) sulfone (**11**). The structure was confirmed by its ^1H NMR spectrum, which displayed a broad singlet at 10.32 for two NH protons and a multiplet between 6.92-7.98 for Ar-H, C_5 -H and C_5' -H (Table 2). The IR spectra of **4-6** and **8-11** showed absorption bands in the region 1575-1590 (C=N), 1325-1360, 1125-1150 (SO_2) and 3330-3350 (NH). In addition to these **4**, **8** and **9** exhibited bands in the region 1610-1625 (C=C). The structures of the compounds **4-6** and **8-11** were further confirmed by ^{13}C NMR spectra (Table 2).

In conclusion, a variety of symmetrical and unsymmetrical bispyrazolines were conveniently prepared by a straightforward successfully established method, 1,3-dipolar cycloaddition of dipolarophile, diazomethane to an activated bisolefin.

Scheme 2

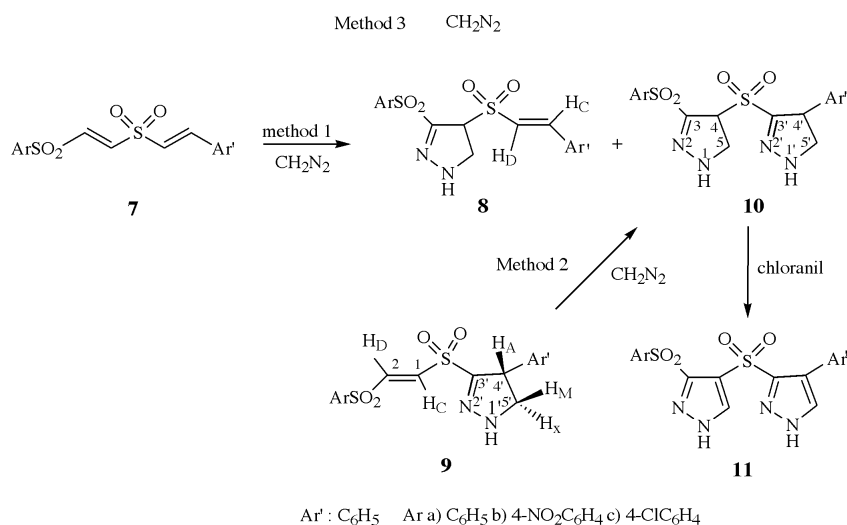


Table 2
Spectroscopic Data of Compounds **4-6** and **8-11**

Compd	^1H NMR (δ , ppm)	^{13}C NMR (δ ppm)
3a	7.28-8.05 (m, 14H, H_a , H_b & Ar-H)	147.84 (C_1), 140.92 (C_2)
3c	7.30-8.12 (m, 12H, H_a , H_b & Ar-H)	146.9 (C_1), 140.50 (C_2)
4a	3.85 (dd, 1H, H_X), 4.42 (dd, 1H, H_M , $J_{MX} = 10.0$), 5.04 (dd, 1H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.68 (d, 1H, H_C , $J_{CD} = 14.2$), 7.02-7.96 (m, 11H, Ar-H & H_D), 10.22 (bs, 1H, N-H)	52.42 (C_4), 58.10 (C_5), 142.14 (C_1') 145.13 (C_2'), 156.40 (C_3)
4c	3.83 (dd, 1H, H_X), 4.49 (dd, 1H, H_M , $J_{MX} = 10.1$), 4.96 (dd, 1H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.65 (d, 1H, H_C , $J_{CD} = 14.2$), 7.10-7.98 (m, 9H, Ar-H & H_D), 10.24 (bs, 1H, N-H)	52.29 (C_4), 58.10 (C_5), 142.82 (C_1') 145.13 (C_2'), 156.41 (C_3)
5a	3.80 (dd, 2H, H_X), 4.49 (dd, 2H, H_M , $J_{MX} = 10.0$), 4.96 (dd, 2H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 7.05- 7.90 (m, 10H, Ar-H), 10.29 (bs, 2H, N-H)	52.82 (C_4 , C_4'), 58.60 (C_5 , C_5'), 158.10 (C_3 , C_3')
5c	3.85 (dd, 2H, H_X), 4.42 (dd, 2H, H_M , $J_{MX} = 10.0$), 5.01 (dd, 2H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 7.05- 7.98 (m, 8H, Ar-H), 10.29 (bs, 2H, N-H)	52.32 (C_4 , C_4'), 59.04 (C_5 , C_5'), 159.30 (C_3 , C_3')
6a	6.98-7.86 (m, 12H, C_5 -H, C_5' -H & Ar-H), 10.34 (bs, 2H, NH)	135.94 (C_5 , C_5'), 140.41 (C_4 , C_4'), 159.10 (C_3 , C_3')
6c	7.04-7.92 (m, 10H, C_5 -H, C_5' -H & Ar-H), 10.30 (bs, 2H, NH)	134.92 (C_5 , C_5'), 141.25 (C_4 , C_4'), 160.12 (C_3 , C_3')
8a	3.82 (dd, 1H, H_X), 4.45 (dd, 1H, H_M , $J_{MX} = 10.0$), 5.04 (dd, 1H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.68 (d, 1H, H_C , $J_{CD} = 14.2$), 6.98- 7.82 (m, 11H, Ar-H & H_D), 10.20 (bs, 1H, N-H)	52.64 (C_4), 58.65 (C_5), 32.58(C_1'), 140.32 (C_2'), 158.23 (C_3).
8c	3.88 (dd, 1H, H_X), 4.53 (dd, 1H, H_M , $J_{MX} = 10.0$), 4.98 (dd, 1H, H_A , $J_{AX} = 5.6$, $J_{AM} = 12.7$), 6.66 (d, 1H, H_C , $J_{CD} = 14.2$), 7.02-7.94 (m, 10H, Ar-H & H_D), 10.22 (bs, 1H, N-H)	52.32 (C_4), 58.05 (C_5), 132.93 (C_1') 142.32 (C_2'), 158.12 (C_3).
9a	3.45 (dd, 1H, H_X), 4.16 (dd, 1H, H_M , $J_{MX} = 10.0$), 4.68 (dd, 1H, H_A , $J_{AX} = 5.6$, $J_{AM} = 12.7$), 6.69 (d, 1 H, H_D , $J_{CD} = 14.3$), 7.04-7.98 (m, 11H, Ar-H & H_C), 10.32 (bs, 1H, N-H)	52.64 (C_4'), 55.02 (C_5'), 141.40 (C_1), 143.53 (C_2), 158.04 (C_3').
9b	3.52 (dd, 1H, H_X), 4.10 (dd, 1H, H_M , $J_{MX} = 10.0$), 4.68 (dd, 1H, H_A , $J_{AX} = 5.6$, $J_{AM} = 12.7$), 6.66 (d, 1H, H_D , $J_{CD} = 14.2$), 7.06-8.01 (m, 10H, Ar-H & H_C), 10.30 (bs, 1H, N-H)	48.32 (C_4'), 55.42 (C_5'), 141.10 (C_1), 144.22 (C_2), 158.50 (C_3').
10a	3.45 (dd, 1H, H_X), 3.88 (dd, 1H, H_X), 4.10 (dd, 1H, H_M' , $J_{M'X'} = 10.0$), 4.45 (dd, 1H, H_M , $J_{MX} = 10.1$), 4.68 (dd, 1H, H_A' , $J_{A'X'} = 5.5$, $J_{A'M'} = 12.6$), 4.98 (dd, 1H, H_A , $J_{AX} = 5.4$, $J_{AM} = 12.6$), 7.02-7.94 (m, 10H, Ar-H), 10.20 (bs, 2H, N-H)	48.28 (C_4'), 52.38 (C_4), 57.45 (C_5 & C_5'), 157.23 (C_3'), 158.40 (C_3)
10c	3.52 (dd, 1H, H_X), 3.82 (dd, 1H, H_X), 4.16 (dd, 1H, H_M' , $J_{M'X'} = 10.0$), 4.53 (dd, 1H, H_M , $J_{MX} = 10.1$), 4.62 (dd, 1H, H_A' , $J_{A'M'} = 12.6$), 5.04 (dd, 1H, H_A , $J_{AX} = 5.5$, $J_{AM} = 12.6$), 7.04-7.98 (m, 9H, Ar-H), 10.22 (bs, 2H, N-H)	48.12 (C_4'), 52.32 (C_4), 57.42 (C_5 & C_5'), 157.20 (C_3'), 158.48 (C_3)
11a	6.92-7.85 (m, 12H, C_5 -H, C_5' -H & Ar-H), 10.32 (bs, 2H, NH)	135.62 (C_5 & C_5'), 140.62 (C_4'), 142.10 (C_4), 157.23 (C_3'), 158.48 (C_3)
11c	6.94-7.98 (m, 11H, C_5 -H, C_5' -H & Ar-H), 10.35 (bs, 2H, NH)	135.10 (C_5 & C_5'), 140.92 (C_4'), 141.18 (C_4), 158.23 (C_3'), 159.82 (C_3)

EXPERIMENTAL

Melting points were determined on Tempo Mel-Temp apparatus and are uncorrected. The IR spectra were recorded on a Perkin - Elmer grating infrared spectrophotometer model 337 as KBr pellets and the wave numbers were given in cm^{-1} . The ^1H NMR spectra were recorded on Bruker Spectrospin 300 MHz spectrometer in CDCl_3 with TMS as an internal standard and the ^{13}C NMR spectra were recorded on a Varian VXR spectrometer operating at 75.5 MHz with CDCl_3 as solvent. Elemental analy-

ses were performed using a Perkin-Elmer 240C elemental analyzer. The chemical shifts were measured in δ ppm. The purity of the compounds was checked by TLC using silica gel 'G' (BDH) and hexane-ethyl acetate as eluents.

1-Arylsulfonyl-2-styrylsulfonylethenes (**7**) were prepared as per the literature procedure [5].

Bis(2-arylsulfonylethenyl)-[1,1']-sulfides (**2**).

To a solution of 10 mmoles of Na_2S in 20 ml of methanol, 20 mmoles of 1-arylsulfonyl-2-chloroethene (**1**) in 20 ml of

methanol was added dropwise with stirring at room temperature for half an hour. The separated solid was collected by filtration, washed with water and recrystallized from methanol.

Bis(2-arylsulfonylethenyl)-[1,1']-sulfones (3).

To a solution of 10 mmoles of **2** in 10 ml of glacial acetic acid, 35 ml of 30% H₂O₂ was added in portions and refluxed for 1-2 hours. The contents were cooled and poured onto crushed ice. The solid obtained was collected by filtration, washed with water and dried. The crude compound was recrystallized from 2-propanol.

Cycloaddition of Diazomethane to **3**.

Method 1.

A solution of 10 mmoles of **3** in 20 ml of dichloromethane was cooled at ice-salt bath temperature. To this 80 ml of 4 M ethereal solution of diazomethane and a catalytic amount of triethylamine was added. The reaction mixture was kept at –20 to –15 °C for 48 hours. The solvent was removed under reduced pressure. The resultant product indicated a mixture in TLC, which were separated by column chromatography using ethyl acetate-hexane (1:3) as eluents and identified as 2'-arylsulfonylethenyl-3-aryl-sulfonyl-2-pyrazoliny-4,1'-sulfone (**4**) and bis(3-arylsulfonyl-2-pyrazoliny-4,4')-sulfone (**5**).

Method 2.

Compound **5** was also obtained when a solution of 10 mmoles of **4** was treated with 40 ml of 4 M ethereal diazomethane and triethylamine. The work up procedure was same as above.

Method 3.

Compound **5** was also prepared by the treatment of 10 mmoles of **3** with 120 ml of 4 M ethereal diazomethane under similar conditions.

Oxidation of **5**.

A solution of 5 mmoles of **5** and 5.2 mmoles of chloranil in 10 ml of xylene was refluxed for 24-32 hours at which time the solution was washed with 5% NaOH solution. The organic layer was separated and repeatedly washed with water, dried and the solvent was removed on a rotary evaporator. The product thus obtained when recrystallized from 2-propanol furnished pure bis (3-arylsulfonylpyrazolyl)-[4,4']-sulfone (**6**).

Cycloaddition of Diazomethane to **7**.

Method 1.

A solution of 10 mmoles of **7** in 20 ml of dichloromethane was cooled at an ice-salt bath temperature. To this, 80 ml of 4 M ethereal diazomethane and a catalytic amount of triethylamine were

added. The reaction mixture was kept at –20 to –15 °C for 48 hours. The solvent was removed under reduced pressure. The resultant product indicated a mixture in TLC, which were separated by column chromatography using ethyl acetate-hexane (1:3) as eluents and identified as 3-arylsulfonyl-2-pyrazoliny-4-styrylsulfone (**8**), 2-arylsulfonylethenyl-4'-aryl-2'-pyrazoliny-1,3'-sulfone (**9**) and 3-arylsulfonyl-2-pyrazoliny-4'-aryl-2'-pyrazoliny-4,3'-sulfone (**10**).

Method 2.

Compound **10** was also obtained when an ethereal solution of **9** was treated with 40 ml of 4 M ethereal diazomethane and triethylamine. The work up procedure was same as above.

Method 3.

Compound **10** was also prepared by the treatment of 10 mmoles of **7** with 120 ml of 4 M ethereal diazomethane under similar conditions.

Oxidation of **10**.

A solution, of 5 mmoles of **10** and 5.2 mmoles of chloranil in 10 ml of xylene, was refluxed for 24-32 hours, at which time the solution was washed with 5% NaOH solution. The organic layer was separated and repeatedly washed with water, dried and the solvent was removed on a rotary evaporator. The solid obtained was purified by recrystallization in 2-propanol to get pure 3-aryl-sulfonylpyrazolyl-4-(4'-arylpyrazolyl) sulfone (**11**).

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