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Studies on Reactivity of Bisolefinic Diketo Sulfides/Sulfones. II

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ABSTRACT

The cycloaddition of diazomethane to *bis*(1-aryl-2-propen-1-one) sulfides/sulfones (**1/2**) and cyclocondensation of **1/2** with hydrazine hydrate has been studied.

Key Words: Cyclocondensation; 1,3-Dipolar cycloaddition; Diazomethane; Hydrazine hydrate.

The chemistry of five membered heterocycles particularly pyrazole and its derivatives possess a wide spectrum of biological properties.[1] During the last one and half decades we have been actively involved in the 1,3-dipolar cycloaddition of ylides and cyclocondensation of

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hydrazine hydrate with Michael acceptors to get 2-pyrazolines.[2] Our recent studies on the cycloaddition of diazomethane to bifunctional olefins, 1-aroyl-2-arylsulfonylethenes and 1,2-*bis*(arylsulfonyl)ethenes under different conditions led to a variety of pyrazolines and pyrazoles.[3] Similarly the reaction of 1-aroyl-2-arylsulfonyl-ethenes with different ratios of hydrazine hydrate gave 2-pyrazolines, hydrazones, and dimerized products.[4] Apart from these, the bifunctional bisolefins, 1-aroyl-2-styrylsulfonylethenes have also been used as a source to obtain novel *bis* pyrazolines/pyrazoles adopting similar methodology.[5] In view of these observations and being undeterred by the results we further examined our study on the reactivity of bisolefinic diketo sulfides/sulfones with diazomethane and hydrazine hydrate.

The synthetic scheme involves the reaction of bis (1-aryl-2-propen-1-one) sulfide/sulfone (**1/2**) with two moles of diazomethane in the presence of triethylamine at −20 to −15°C (Sch. 1, Table 1). When the progress of the reaction was monitored at frequent intervals two spots were observed in TLC which persisted even after 48 h. The two were separated by column chromatography and identified as 3-aroyl-2-pyrazolinyl-2′-aroyl-ethenyl-[4,1′]-sulfide/sulfone (**3/4**) as a major product and *bis*(3,3′-aroyl-2-pyrazolinyl)-[4,4′]-sulfide/sulfone (**5/6**) as a minor one.

The ^{1}H NMR spectra of **3/4** indicated an AMX splitting pattern for methine and methylene protons of pyrazoline ring. Thus, three double doublets observed in **3a** at 4.70 ($J_{AM} = 12.6$, $J_{AX} = 5.5$) at 3.92 ($J_{MX} = 10.0$) and at 3.52 was assigned to H_A, H_M and H_X, respectively. However, **4a** exhibited double doublets at 4.71 ($J_{AM} = 12.6$, $J_{AX} = 5.6$), 3.93 ($J_{MX} = 10.1$) and 3.58 which was attributed to H_A, H_M and H_X, respectively. The J values indicate that H_A, H_M and H_A, H_X are *cis* and *trans* oriented while H_M, H_X are *geminal*. The olefinic proton, H_C showed a doublet at 6.60 in **3a** and at 6.66 in **4a** whereas H_D merged with aromatic protons and appeared as a multiplet. The coupling constant of ethylenic protons indicated that they possess *trans* geometry. A broad singlet in the region 10.12 in **3a** and 10.14 in **4a** was observed for N-H proton, which disappeared on deuteration.

However, when **1/2** was treated with excess diazomethane in the presence of triethylamine at −20°C to −15°C resulted only **5/6**. The latter was also obtained by the cycloaddition of one mole of diazomethane to **3/4** under similar reaction conditions. The two pyrazoline ring protons in their ^{1}H NMR spectra showed AMX splitting pattern as in **3/4** and exhibited their resonance signals almost in the same region (Table 2).

On the other hand, cyclocondensation of **1/2** with hydrazine hydrate in ethanol afforded 3-aryl-2-pyrazolinyl-2′-aroylethenyl-[5,1′]-sulfide/sulfone (**7/8**) as major and *bis*(3,3′-aryl-2-pyrazolinyl)-[5,5′]-sulfide/sulfone

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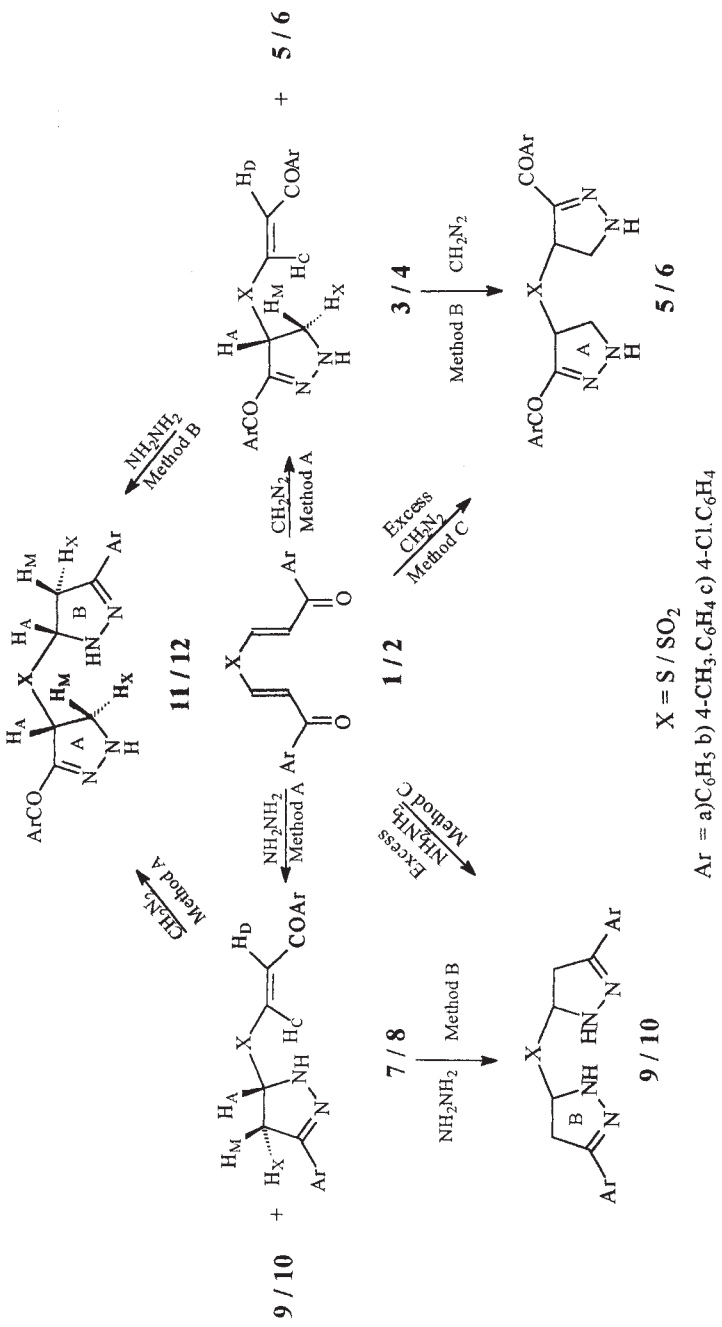

Scheme 1.

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Table 1. Physical data of compounds **1–12**.

Compd. no.	M.p. (°C)	Yield (%)	Mol. formula Mol. wt.	Found(calcd.) % C	H	N
1a	192–194	60	$C_{18}H_{14}O_2S$ (294.38)	—	—	—
1b	204–206	65	$C_{20}H_{18}O_2S$ (322.43)	—	—	—
1c	210–212	70	$C_{18}H_{12}Cl_2O_2S$ (363.27)	—	—	—
2a	220–214	68	$C_{18}H_{14}O_4S$ (326.37)	—	—	—
2b	212–214	63	$C_{20}H_{18}O_4S$ (354.43)	—	—	—
2c	221–223	72	$C_{18}H_{12}Cl_2O_4S$ (395.26)	—	—	—
3a	112–114	62	$C_{19}H_{16}N_2O_2S$ (336.42)	67.95 (67.84)	4.71 (4.79)	8.24 (8.33)
3b	96–98	58	$C_{21}H_{20}N_2O_2S$ (364.47)	69.07 (69.21)	5.44 (5.53)	7.83 (7.69)
3c	128–130	69	$C_{19}H_{14}Cl_2N_2O_2S$ (405.31)	56.46 (56.31)	3.57 (3.48)	6.78 (6.91)
4a	121–122	61	$C_{19}H_{16}N_2O_4S$ (368.41)	61.79 (61.94)	4.42 (4.38)	7.48 (7.60)
4b	104–106	64	$C_{21}H_{20}N_2O_4S$ (396.47)	63.75 (63.62)	5.01 (5.08)	7.17 (7.07)
4c	136–137	66	$C_{19}H_{14}Cl_2N_2O_4S$ (437.30)	52.31 (52.19)	3.14 (3.23)	6.53 (6.41)
5a	156–158	17 75[a] 62[b]	$C_{20}H_{18}N_4O_2S$ (378.46)	63.34 (63.47)	4.87 (4.79)	14.69 (14.80)
5b	163–165	18 73[a] 64[b]	$C_{22}H_{22}N_4O_2S$ (406.51)	65.14 (65.00)	5.37 (5.46)	13.97 (13.78)
5c	172–174	20 77[a] 68[b]	$C_{20}H_{16}Cl_2N_4O_2S$ (447.35)	53.79 (53.70)	3.68 (3.61)	12.64 (12.52)
6a	164–166	21 78[a] 60[b]	$C_{20}H_{18}N_4O_4S$ (410.45)	58.65 (58.53)	4.35 (4.42)	13.73 (13.65)
6b	167–168	19 70[a] 61[b]	$C_{22}H_{22}N_4O_4S$ (438.51)	60.39 (60.26)	5.14 (5.06)	12.88 (12.78)
6c	172–174	20 80[a] 66[b]	$C_{20}H_{16}Cl_2N_4O_4S$ (479.34)	49.98 (50.11)	3.29 (3.36)	11.83 (11.69)
7a	102–104	65	$C_{18}H_{16}N_2OS$ (308.41)	70.24 (70.10)	5.16 (5.23)	9.20 (9.08)
7b	87–89	60	$C_{20}H_{20}N_2OS$ (336.46)	71.29 (71.40)	5.81 (5.99)	8.44 (8.33)

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Table 1. Continued.

Compd. no.	M.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Found(calcd.) % C	H	N
7c	112–114	67	$C_{18}H_{14}Cl_2N_2OS$ (377.30)	57.45 (57.30)	3.67 (3.74)	7.31 (7.42)
8a	116–118	63	$C_{18}H_{16}N_2O_3S$ (340.40)	63.38 (63.51)	4.82 (4.74)	8.11 (8.23)
8b	100–102	60	$C_{20}H_{20}N_2O_3S$ (368.46)	65.06 (65.20)	5.56 (5.47)	7.49 (7.60)
8c	132–134	68	$C_{18}H_{14}Cl_2N_2O_3S$ (409.29)	52.94 (52.82)	3.52 (3.45)	6.93 (6.84)
9a	140–142	20 76[a] 72[b]	$C_{18}H_{18}N_4S$ (322.43)	67.19 (67.05)	5.54 (5.63)	17.26 (17.38)
9b	128–130	18 78[a] 69[b]	$C_{20}H_{22}N_4S$ (350.49)	68.41 (68.54)	6.42 (6.33)	15.87 (15.99)
9c	136–138	21 73[a] 71[b]	$C_{18}H_{16}Cl_2N_4S$ (391.33)	55.39 (55.25)	4.03 (4.12)	14.45 (14.32)
10a	158–160	22 71[a] 65[b]	$C_{18}H_{18}N_4O_2S$ (354.43)	61.14 (61.00)	5.04 (5.12)	15.73 (15.81)
10b	164–166	19 76[a] 74[b]	$C_{20}H_{22}N_4O_2S$ 382.49	62.93 (62.81)	5.85 (5.80)	14.76 (14.65)
10c	173–175	24 80[a] 75[b]	$C_{18}H_{16}Cl_2N_4O_2S$ (423.32)	51.20 51.07	3.73 (3.81)	13.36 (13.23)
11a	138–140	64 70[a]	$C_{19}H_{18}N_4OS$ (350.45)	65.26 (65.12)	5.09 (5.18)	16.07 (15.99)
11b	126–128	62 78[a]	$C_{21}H_{22}N_4OS$ (378.50)	66.50 (66.64)	5.80 (5.86)	14.90 (14.80)
11c	142–144	65 76[a]	$C_{19}H_{16}Cl_2N_4OS$ (419.34)	54.31 (54.42)	3.92 (3.85)	13.24 (13.36)
12a	158–160	64 73[a]	$C_{19}H_{18}N_4O_3S$ (382.45)	59.81 (59.67)	4.67 (4.74)	14.72 (14.65)
12b	163–165	68 70[a]	$C_{21}H_{22}N_4O_3S$ (410.50)	61.31 (61.45)	5.31 (5.40)	13.77 (13.65)
12c	174–176	65 76[a]	$C_{19}H_{16}\ Cl_2N_4O_3S$ (451.33)	50.42 (50.56)	3.49 (3.57)	12.53 (12.41)

Satisfactory elemental analysis were obtained for the representative samples: C ± 0.24; H ± 0.15; N ± 0.22.

[a]From Method B.

[b]From Method C.

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Table 2. ^{1}H NMR spectral data of compounds **3–12**.

Compd. no.	^{1}H NMR δ ($CDCl_3$), ppm
3a	3.52 (dd, 1H, H_X), 3.92 (dd, 1H, H_M, $J_{MX} = 10.0$), 4.70 (dd, 1H, H_A, $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.60 (d, 1H, H_C, $J_{CD} = 14.2$), 6.92–8.15 (m, 11H, H_D and Ar-H), 10.18 (bs, 1H, NH)
3b	2.25 (s, 6H, Ar-CH_3), 3.54 (dd, 1H, H_X), 3.94 (dd, 1H, H_M, $J_{MX} = 10.0$), 4.76 (dd, 1H, H_A, $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.62 (d, 1H, H_C, $J_{CD} = 14.2$), 6.94–8.17 (m, 9H, H_D and Ar-H), 10.16 (bs, 1H, NH)
4a	3.58 (dd, 1H, H_X), 3.93 (dd, 1H, H_M, $J_{MX} = 10.1$), 4.71 (dd, 1H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 6.66 (d, 1H, H_C, $J_{CD} = 14.2$), 7.01–8.12 (m, 11H, H_D, and Ar-H), 10.14 (bs, 1H, NH)
4c	3.64 (dd, 1H, H_X), 3.99 (dd, 1H, H_M, $J_{MX} = 10.2$), 4.54 (dd, 1H, H_A, $J_{AX} = 5.1$, $J_{AM} = 11.7$), 6.64 (d, 1H, H_C, $J_{CD} = 14.2$), 7.01–8.10 (m, 9H, H_D and Ar-H) 10.15 (bs, 1H, NH)
5a	3.55 (dd, 2H, H_X), 3.92 (dd, 2H, H_M, $J_{MX} = 10.1$), 4.76 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 6.92–7.89 (m, 10H, Ar-H), 10.20 (bs, 2H, NH)
5c	3.58 (dd, 2H, H_X), 3.98 (dd, 2H, H_M, $J_{MX} = 10.5$), 4.72 (dd, 2H, H_A, $J_{AX} = 5.5$, $J_{AM} = 12.6$), 7.10–7.85 (m, 8H, Ar-H), 10.24 (bs, 2H, NH)
6a	3.60 (dd, 2H, H_X), 4.10 (dd, 2H, H_M, $J_{MX} = 10.5$), 4.78 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 6.90–7.86 (m, 10H, Ar-H), 10.22 (bs, 2H, NH)
6b	2.25 (s, 6H, Ar-CH_3), 3.52 (dd, 2H, H_X), 4.12 (dd, 2H, H_M, $J_{MX} = 10.5$), 4.76 (dd, 2H, H_A, $J_{AX} = 5.5$, $J_{AM} = 12.6$), 6.92–7.86 (m, 8H, Ar-H), 10.25 (bs, 2H, NH)
7a	2.96 (dd, 1H, H_X), 3.65 (dd, 1H, H_M, $J_{MX} = 16.8$), 5.60 (dd, 1H, H_A, $J_{AX} = 5.5$, $J_{AM} = 11.7$), 6.62 (d, 1H, H_C, $J_{CD} = 14.2$), 7.00–8.12 (m, 11H, H_D, and Ar-H), 10.08 (bs, 1H, NH)
7c	2.98 (dd, 1H, H_X), 3.68 (dd, 1H, H_M, $J_{MX} = 16.9$), 5.62 (dd, 1H, H_A, $J_{AX} = 5.5$, $J_{AM} = 11.7$), 6.61 (d, 1H, H_C, $J_{CD} = 14.2$), 7.12–8.14 (m, 9H, H_D, and ArH), 10.10 (bs, 1H, NH)
8a	2.96 (dd, 1H, H_X), 3.78 (dd, 1H, H_M, $J_{MX} = 17.1$), 5.70 (dd, 1H, H_A, $J_{AX} = 5.55$, $J_{AM} = 12.0$), 6.78 (d, 1H, H_C, $J_{CD} = 14.2$), 7.10–8.16 (m, 11H, H_D, and Ar-H), 10.10 (bs, 1H, NH)
8c	3.02 (dd, 1H, H_X), 3.72 (dd, 1H, H_M, $J_{MX} = 16.8$), 5.68 (dd, 1H, H_A, $J_{AX} = 5.5$, $J_{AM} = 11.7$), 6.78 (d, 1H, H_C, $J_{CD} = 14.2$), 7.14–8.20 (m, 9H, H_D, and Ar-H), 10.12 (bs, 1H, NH)
9a	2.99 (dd, 2H, H_X), 3.72 (dd, 2H, H_M, $J_{MX} = 16.9$), 5.65 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 11.8$), 6.92–7.89 (m, 10H, Ar-H), 10.00 (bs, 2H, NH)

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Table 2. Continued.

Compd. no.	^{1}H NMR δ ($CDCl_3$), ppm
9c	2.95 (dd, 2H, H_X), 3.82 (dd, 2H, H_M, $J_{MX} = 17.0$), 5.66 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 11.7$), 6.95–7.90 (m, 8H, Ar-H), 10.20 (bs, 2H, NH)
10a	2.92 (dd, 2H, H_X), 3.80 (dd, 2H, H_M, $J_{MX} = 16.9$), 5.76 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 11.9$), 6.95–7.89 (m, 10H, Ar-H), 9.96 (bs, 2H, NH)
10c	2.97 (dd, 2H, H_X), 3.81 (dd, 2H, H_M, $J_{MX} = 17.0$), 5.78 (dd, 2H, H_A, $J_{AX} = 5.6$, $J_{AM} = 11.7$), 6.98–7.92 (m, 8H, Ar-H), 10.21 (bs, 2H, NH)
11a	2.96 (dd, 1H, H_X'), 3.42 (dd, 1H, H_X), 3.74 (dd, 1H, H_M' $J_{M'X'} = 16.7$), 4.10 (dd, 1H, H_M $J_{MX} = 10.6$), 4.72 (dd, 1H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 5.68 (dd, 1H, H_A' $J_{A'X'} = 5.6$, $J_{A'M'} = 11.8$), 6.92–8.10 (m, 10H, Ar-H), 9.92 (bs, 1H, NH), 10.20 (bs, 1H, NH)
11b	2.24 (s, 6H, Ar-CH_3), 2.98 (dd, 1H, H_X'), 3.40 (dd, 1H, H_X), 3.72 (dd, 1H, H_M', $J_{A'X'} = 17.1$), 4.11 (dd, 1H, H_M, $J_{MX} = 10.60$), 4.75 (dd, 1H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 5.64 (dd, 1H, H_A', $J_{A'X'} = 5.6$, $J_{A'M'} = 11.8$), 7.10–8.14 (m, 8H, Ar-H), 9.96 (bs, 1H, NH), 10.24 (bs, 1H, NH)
12a	3.02 (dd, 1H, H_X'), 3.40 (dd, 1H, H_X), 3.74 (dd, 1H, H_M', $J_{M'X'} = 16.8$), 4.00 (dd, 1H, H_M, $J_{MX} = 10.6$), 4.72 (dd, 1H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 5.76 (dd, 1H, H_A', $J_{A'X'} = 5.6$, $J_{A'M'} = 11.7$), 6.90–8.14 (m, 10H, Ar-H), 10.00 (bs, 1H, NH), 10.22 (bs, 1H, NH)
12b	2.28 (s, 6H, Ar-CH_3), 3.10 (dd, 1H, H_X'), 3.42 (dd, 1H, H_X), 3.78 (dd, 1H, H_M', $J_{M'X'} = 17.1$), 4.12 (dd, 1H, H_M, $J_{MX} = 10.6$), 4.76 (dd, 1H, H_A, $J_{AX} = 5.6$, $J_{AM} = 12.6$), 5.78 (dd, 1H, H_A', $J_{A'X'} = 5.6$, $J_{A'M'} = 11.7$), 6.92–7.91 (m, 8H, Ar-H), 10.00 (bs, 1H, NH), 10.24 (bs, 1H, NH)

(**9/10**) as minor one. The methine and methylene protons of pyrazoline ring in **7/8** also exhibited AMX splitting pattern. Thus three double doublets were observed in the spectra of **7a** at 5.60 (H_A), 3.65 (H_M) and 2.96 (H_X) with coupling constants $J_{AM} = 11.7$, $J_{MX} = 16.8$, and $J_{AX} = 5.5$ and in **8a** at 5.70 (H_A), 3.78 (H_M) and 2.96 (H_X) with coupling constants $J_{AM} = 11.8$, $J_{MX} = 16.9$ and $J_{AX} = 5.5$. The H_C showed a doublet at 6.62 ($J_{CD} = 14.2$) in **7a** and at 6.78 ($J_{CD} = 14.2$) in **8a** while H_D merged with aromatic protons and appeared as a multiplet. The **7/8** on further treatment with hydrazine hydrate gave **9/10**, which was also

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obtained directly from **1/2** with excess hydrazine hydrate. The two pyrazoline ring protons in **9/10** showed similar type of splitting pattern as in **7/8** in their ^{1}H NMR spectra (Table 2). On the other hand **3/4** with hydrazine hydrate furnished 3-aroyl-3′-aryl-*bis*-(2-pyrazolinyl)-[4,5′]-sulfide/sulfone (**11/12**), which has two different pyrazoline rings as evidenced by their ^{1}H NMR. The latter were also obtained by the treatment of **7/8** with diazomethane. Interestingly enough in **11/12**, the protons H_A, H_M, and H_X of ring A exhibited resonance signals almost in the same region as in **3–6** while ring B protons as in **7–10**. The authenticity of bis pyrazolines obtained by different routes was confirmed by ^{1}H NMR and m.mp. The IR spectra of **3–12** showed absorption bands in the regions 1565–1575 (C = N), 3330–3350 (NH). Apart from these **4**, **6**, **8**, **10**, and **12** displayed bands around 1325–1350, 1130–1150 (SO_2), **3**, **4**, **7**, **8** in the region 1610–1620 (C = C) and **3–8**, **11**, **12** around 1660–1685 (C = O).

In conclusion, a novel type of bis pyrazolines have been developed from *bis*(1-aryl-2-propen-1-one) sulfide/sulfone by either 2 + 3 and/or 3 + 2 cyclization of diazomethane and hydrazine hydrate.

EXPERIMENTAL

Melting points were determined on Tempo Mel-Temp apparatus and were uncorrected. The IR spectra were recorded on a Perkin-Elmer grating Infrared spectrophotometer model 337 as KBr pellets and the wave numbers were in cm^{-1}. The ^{1}H NMR spectra were recorded on Bruker spectrospin 300 MHz spectrometer in $CDCl_3$ with TMS as an internal standard and the chemical shifts were measured in ppm. The purity of the compounds was checked by TLC using silica gel 'G' (BDH) and hexane-ethyl acetate as eluents. Microanalyses were performed by the Regional Sophisticated Instrumentation Centre, Punjab University, Chandigarh, India.

bis(1-Aryl-2-propen-1-one)-3,3′-sulfide (1)

General Procedure

To a solution of 10 mmol of Na_2S in 20 mL of methanol, 20 mmol of 1-aroyl-2-chloroethane in 20 mL of methanol was added dropwise with stirring at room temperature for half an hour. The separated solid was filtered, washed with water and recrystallized from methanol to get **1**.

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bis(1-Aryl-2-propen-1-one)-3,3′-sulfone (2)

General Procedure

To a solution of 10 mmoles of **1** in 20 mL of glacial acetic acid, 35 mL of 30% hydrogen peroxide was added in portions and refluxed for 1–2 h. The contents were cooled and poured onto crushed ice. The solid obtained was filtered, washed with water and dried. The crude compound was recrystallized from 2-propanol.

3-Aroyl-2-pyrazolinyl-2′-aroylethenyl-[4,1′]-sulfide/sulfone (3/4) and *bis*(3,3′-Aroyl-2-pyrazolinyl)-[4,4′]-sulfide/sulfone (5/6)

General Procedure

Method A. A solution of 10 mmoles of **1/2** in 20 mL of dichloromethane was cooled at an 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°C to -15°C for 48 h. 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 **3/4** and **5/6**.

Method B. The compounds **5/6** were also obtained when a solution of 10 mmoles of **3/4** was treated with 40 mL of 4 M ethereal diazomethane and triethylamine. The work-up procedure was same as above.

Method C. The compounds **5/6** were also prepared by the treatment of 10 mmoles of **1/2** with 120 mL of 4 M ethereal diazomethane under similar conditions.

3-Aryl-2-pyrazolinyl-2′-aroylethenyl-[5,1′]-sulfide/sulfone (7/8) and *bis*(3,3′-Aryl-2-pyrazolinyl)-[5,5′]-sulfide/sulfone (9/10)

General Procedure

Method A. A mixture of 10 mmoles of **1/2**, 25 mmoles of 80% hydrazine hydrate in 20 mL of ethanol was refluxed for 2–3 h. The reaction mixture was cooled and poured onto crushed ice. The solid obtained was

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filtered and dried. The crude compound indicated two spots in TLC which were separated by column chromatography and identified as **7/8** and **9/10**.

Method B. The **9/10** were also obtained by the treatment of 10 mmoles of **7/8** with 15 mmoles of 80% hydrazine hydrate. The resultant solid was purified by recrystallization from ethanol.

Method C. The compounds **1/2** with 30 mmoles of 80% hydrazine hydrate under above conditions afforded only **9/10** which was purified by recrystallization from ethanol.

3-Aroyl-3′-aryl-*bis*-(2-pyrazolinyl)-[4,5′]-sulfide/sulfone (11/12)

Method A. To a solution of 10 mmoles of **7/8** in 20 mL of dichloromethane 40 mL of ethereal diazomethane and a catalytic amount of triethylamine was added. The reaction mixture was kept at -20°C to -15°C for 48 h. This on work up afforded a product, **11/12**, which was recrystallized from ethanol.

Method B. The **11/12** was also obtained by refluxing 10 mmoles of **3/4** and 15 mmoles of 80% hydrazine hydrate in 20 mL of ethanol for 2–3 h. The solid separated was filtered and recrystallized from ethanol.

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