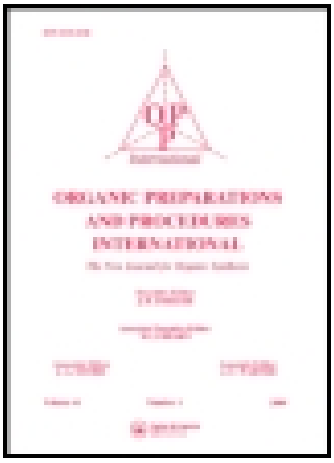

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CYCLOPROPYL AND PYRAZOLYL SELENADIAZOLYL AND THIADIAZOLYL SULFONES AND THEIR REACTIVITY

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CYCLOPROPYL AND PYRAZOLYL SELENADIAZOLYL AND THIADIAZOLYL SULFONES AND THEIR REACTIVITY

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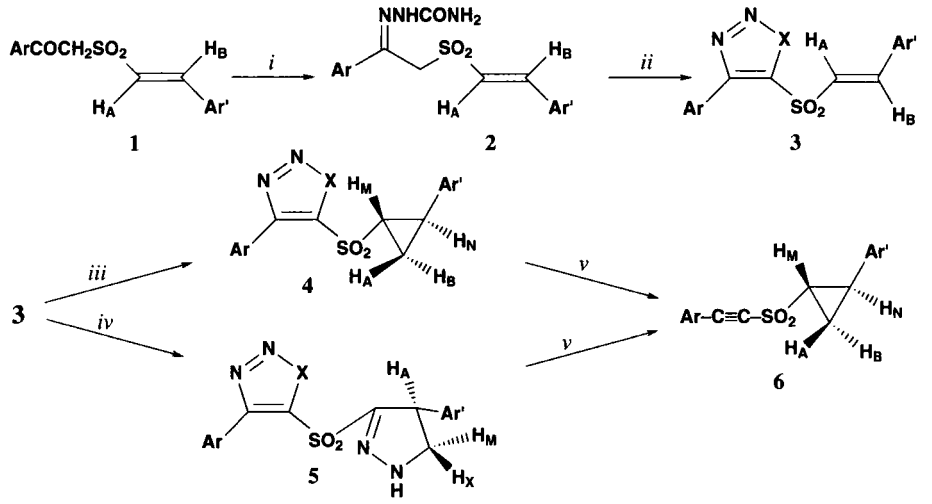
As part of our ongoing study of the chemistry of heterocycles, phenacyl bromides have been utilized as key intermediates for thiomorpholines[1] and pyrazolines.[2] We now report that the synthetic utility of phenacyl bromides has been extended further to prepare phenacylstyryl sulfones. These sulfones serve as precursors for the elaboration of two different rings within the same molecule, leading to novel systems. It is well known that pyrazolines on pyrolysis give cyclopropanes while selenadiazoles lead to alkynes. We felt it desirable to synthesize molecules having bifunctional systems, *viz.*, cyclopropyl and alkynyl moieties and to study their chemistry.

Our synthetic scheme involves the condensation of phenacyl bromides with styryl sulfinates to give phenacyl-E-styryl sulfones **1**.[1] The -CH_2CO- functionality in the latter compounds has been exploited by cyclization of semicarbazones **2** with selenium dioxide or thionyl chloride to afford 4-aryl-5-styrylsulfonyl-1,2,3-selena/thiadiazoles **3**. This result suggests that this type of cyclization is possible only in compounds having methyl or methylene groups α to the keto group.[3] The ethylenic center present in **3** has been utilized to construct cyclopropane and pyrazoline rings.[4,5] Treatment of **3** with dimethylsulfoxonium methylide under phase-transfer catalysis (PTC) conditions afforded 4-aryl-5-(2'-arylcyclopropylsulfonyl)-1,2,3-selena or thiadiazoles **4**. On the other hand, cycloaddition of diazomethane to **3** gave 4-aryl-5-(4'-aryl-3'-sulfonyl-2'-pyrazolyl)-1,2,3-selena/thiadiazoles **5**. The lability of 1,2,3-selenadiazoles and pyrazolines has been noteworthy because of their usefulness as precusors for alkynes[6] and cyclopropanes.[7] Thus the pyrolysis of **4a-g** and **5a-g** gave arylethynyl aryl-cyclopropyl sulfones **6**, a new class of alkyne systems.

The structures of **2-6** were confirmed by analytical and spectroscopic data (Tables 1-5). The IR spectra of **2-6** exhibited bands in the regions 1320 and 1115 cm^{-1} for the sulfonyl group while **2** and **3** showed a band near 1620 for the styryl moiety. Furthermore, compounds **2** displayed bands in the region 3445, 3240 and 1720 characteristic of *NH*CO, CO*NH*$_2$ and *CO*NH_2 groups. The absence of these bands in **3** and the presence of an absorption band at 1440 for N=N indicates that the active methylene group and semicarbazone moiety in **2** are involved in the cyclization processes. The absence of a band in the region 1620 in **4** and the presence of an absorption band around 1020 cm^{-1}



a) Ar = C_6H_5, Ar' = C_6H_5, X = Se
b) Ar = 4-$MeOC_6H_4$, Ar' = C_6H_5, X = Se
c) Ar = 4-ClC_6H_4, Ar' = C_6H_5, X = Se
d) Ar = C_6H_5, Ar' = 4-MeC_6H_4, X = Se
e) Ar = 4-MeC_6H_4, Ar' = 4-MeC_6H_4, X = Se
f) Ar = 4-BrC_6H_4, Ar' = 4-MeC_6H_4, X = Se
g) Ar = 4-$NO_2C_6H_4$, Ar' = 4-MeC_6H_4, X = S
h) Ar = C_6H_5, Ar' = C_6H_5, X = S
I) Ar = 4-$MeOC_6H_4$, Ar' = C_6H_5, X = S
j) Ar = 4-ClC_6H_4, Ar' = C_6H_5, X = S
k) Ar = C_6H_5, Ar' = 4-MeC_6H_4, X = S
l) Ar = 4-MeC_6H_4, Ar' = 4-MeC_6H_4, X = S
m) Ar = 4-BrC_6H_4, Ar' = 4-MeC_6H_4, X = S
n) Ar = 4-$NO_2C_6H_4$, Ar' = 4-MeC_6H_4, X = S

i) $NH_2CONHNH_2$. HCl, NaOAC, MeOH *ii*) SeO_2, AcOH or $SOCl_2$, CH_2Cl_2
iii) $(CH_3)_3$ S(O)I, 50% NaOH, BTEAC, CH_2Cl_2 *iv*) CH_2N_2, $(C_2H_5)_2O$, TEA, -20°
v) Copper powder, 200°

characteristic of cyclopropane ring deformation mode[4] showed that the cyclopropanation indeed has occurred at the activated double bond. Moreover, bands around 1600 and 3310 cm^{-1} in **5** for C=N and NH groups clearly indicate that the cycloaddition of diazomethane to the unsaturated system has been accomplished in a similar way.

The ^1H NMR spectra of **2** and **3** exhibited a doublet for H_A while the signal due to H_B is merged with aromatic protons.[4] The J value (J_{AB} = 15.5 Hz) indicates *trans*-geometry (see Table 1). The absence of a singlet corresponding to CH_2 in **3** indicate that the active methylene group in **2** is involved in cyclization (see Table 2). Compounds **4** and **6** exhibited the ABMN splitting pattern for methylene and methine protons of cyclopropyl ring[8] (see Table 3). Although in general, each group should display doublet of a double doublet as a result of vicinal and geminal couplings, a multiplet is observed. Based on the chemical shift values indicated in the spectra, the approximate values of J_{MN} were calculated. With regard to the methine protons H_M and H_N, H_N appeared downfield as it experiences more deshielding than H_M. On the other hand, of the two methylene protons H_A and H_B, H_A appeared upfield since it is *cis* to the aryl moiety.[9] The pyrazoline ring protons in **5** displayed an AMX pattern[10] and each proton appeared as a doublet of doublet (see Table 4). Proton H_A was observed downfield compared to H_M and H_X. Proton H_A being a methine proton generally experiences a down-

field shift compared to methylene protons H_M and H_X. Furthermore, the former is adjacent to aryl moiety and hence shows a downfield shift. As a result of the deshielding effect of the phenyl moiety on H_M, it appears downfield from H_X. The J values showed that the H_A, H_M and H_A, H_X are *cis* and *trans* oriented, respectively, while H_M, H_X are *geminal*.

TABLE 1. Yields, mps and ^{1}H NMR Data of Compounds **2**

Cmpd	Yield (%)	mp. (°C)	^{1}H NMR δ (ppm) CH_2 (s)	H_A (d)	J_{AB} (Hz)	Ar H + H_B (m)	NH (s)
2a	75	186-187	4.58	6.80	15.5	7.10-7.90	9.45
2b	70	206-208	4.57	6.82	15.5	7.08-7.94	9.30
2c	68	212-214	4.50	6.65	15.2	7.10-7.72	9.25
2d	81	180-181	4.52	6.80	15.2	7.04-7.95	9.27
2e	83	204-205	—	—	—	—	—
2f	79	208-210	4.56	6.70	15.4	7.02-7.83	9.32
2g	82	182-183	4.74	7.08	15.5	7.20-8.05	9.28

TABLE 2. Physical and Spectral Data of Compounds **3**

Cmpd	Yield (%)	mp. (°C)	IR (KBr) cm^{-1} N=N
3a	74	62-63	1440
3b	72	108-109	1438
3c	75	90-91	1445
3d	68	130-131	1440
3e	65	120-121	1442
3f	73	135-136	1448
3g	62	145-146	1445
3h	78	160-161	1435
3i	65	180-181	1420
3j	72	148-149	1425
3k	66	170-171	1430
3l	68	140-141	1428
3m	65	110-111	1420
3n	70	174-175	1425

TABLE 3. Physical and Spectral Data of Compounds **4**

Cmpd	Yield (%)	mp. (°C)	^{1}H NMR δ (ppm) H_A (m)	H_B (m)	H_M (m)	H_N (m)	J_{MN} (Hz)
4a	65	102-103	1.28-1.34	1.59-1.70	2.39-2.45	2.48-2.62	4.98
4b	60	124-125	1.24-1.31	1.57-1.69	2.38-2.46	2.50-2.63	4.95
4c	68	127-128	1.30-1.38	1.60-1.71	2.44-2.53	2.58-2.67	4.99
4d	62	144-146	1.29-1.36	1.55-1.67	2.40-2.48	2.53-2.64	4.98
4e	60	137-138	—	—	—	—	—
4f	65	154-155	1.32-1.40	1.64-1.73	2.43-2.49	2.55-2.65	5.02
4g	62	159-160	—	—	—	—	—
4h	72	165-166	1.30-1.38	1.62-1.73	2.36-2.49	2.52-2.60	5.02
4i	66	192-193	1.29-1.38	1.58-1.69	2.40-2.50	2.55-2.64	5.01
4j	62	155-156	1.32-1.41	1.65-1.75	2.41-2.52	2.58-2.67	5.00
4k	65	185-187	1.27-1.35	1.60-1.71	2.38-2.48	2.54-2.63	5.01
4l	63	167-168	—	—	—	—	—
4m	60	144-145	1.34-1.42	1.66-1.74	2.44-2.53	2.60-2.68	5.02
4n	64	185-187	—	—	—	—	—

TABLE 4. Physical and Spectral Data of Compounds **5**

Cmpd	Yield (%)	mp (°C)	^{1}H NMR δ (ppm) H_A (dd)	H_M (dd)	Hx (dd)	J_{AM} (Hz)	J_{AX} (Hz)	J_{MX} (Hz)
5a	61	172-173	4.52	3.99	3.61	11.0	5.5	10.5
5b	65	203-205	4.48	3.85	3.52	11.0	5.7	10.6
5c	68	195-196	4.50	4.02	3.58	11.2	5.5	10.6
5d	60	220-222	4.45	3.94	3.55	11.2	5.6	10.5
5e	65	210-212	—	—	—	—	—	—
5f	66	228-230	4.49	3.85	3.54	11.2	5.7	10.5
5g	62	196-197	—	—	—	—	—	—
5h	65	257-259	4.50	3.95	3.64	11.1	5.5	10.6
5i	68	274-276	4.45	3.97	3.59	11.0	5.5	10.5
5j	72	212-213	4.53	3.99	3.74	11.1	5.6	10.5
5k	64	270-272	4.50	3.92	3.60	11.0	5.5	10.6
5l	66	202-204	—	—	—	—	—	—
5m	62	195-196	4.52	3.96	3.67	11.0	5.5	10.6
5n	65	271-273	—	—	—	—	—	—

TABLE 5. Physical Data of Compounds **6**

Cmpd	Yield (%) from **5**	Yield (%) from **7**	mp. (°C)
6a	70	55	90-91
6b	63	56	113-114
6c	68	54	119-120
6d	66	53	125-126
6e	65	55	129-130
6f	62	50	137-138
6g	69	52	140-141

TABLE 6. Microanalytical Data of Compounds **2** to **6**

Cmpd	Found (Calcd)		
	C	H	N
2a	59.67 (59.45)	5.03 (4.98)	12.12 (12.23)
2b	60.86 (60.65)	5.48 (5.41)	11.58 (11.68)
2c	54.18 (54.03)	4.30 (4.26)	11.00 (11.12)
2d	60.14 (60.31)	5.42 (5.30)	11.94 (11.79)
2e	61.73 (61.43)	5.87 (5.69)	11.46 (11.31)
2f	49.67 (49.54)	4.21 (4.15)	9.75 (9.63)
2g	53.61 (53.72)	4.42 (4.50)	13.73 (13.92)
3a	51.12 (51.20)	3.32 (3.22)	7.55 (7.46)
3b	52.30 (52.43)	3.48 (3.62)	7.12 (7.21)
3c	47.01 (46.89)	2.75 (2.70)	6.71 (6.85)
3d	52.30 (52.43)	3.58 (3.62)	7.14 (7.21)
3e	53.70 (53.58)	4.09 (3.99)	7.03 (6.96)
3f	43.52 (43.60)	2.68 (2.79)	5.85 (5.99)
3g	47.12 (47.01)	3.10 (3.01)	9.87 (9.67)
3h	58.72 (58.50)	3.70 (3.68)	8.67 (8.55)
3i	59.47 (59.61)	4.31 (4.11)	8.09 (8.20)
3j	53.20 (52.95)	3.00 (3.05)	7.61 (7.74)
3k	59.29 (59.48)	4.03 (4.15)	8.31 (8.12)
3l	60.99 (60.76)	4.67 (4.57)	7.72 (7.60)
3m	48.57 (48.45)	3.12 (3.10)	6.56 (6.66)
3n	52.39 (52.56)	3.25 (3.37)	10.97 (10.81)

TABLE 6. Continued…

Cmpd	Found (Calcd)		
	C	H	N
4a	52.55 (52.43)	3.65 (3.62)	7.30 (7.21)
4b	53.44 (53.58)	4.14 (3.99)	6.85 (6.96)
4c	48.00 (48.17)	3.19 (3.09)	6.60 (6.62)
4d	53.74 (53.58)	4.07 (3.99)	7.08 (6.96)
4e	54.74 (54.66)	4.28 (4.34)	6.80 (6.72)
4f	44.70 (44.82)	3.20 (3.13)	5.80 (5.82)
4g	48.37 (48.22)	3.32 (3.37)	9.51 (9.37)
4h	59.67 (59.61)	4.20 (4.11)	8.29 (8.20)
4i	60.84 (60.63)	4.34 (4.52)	7.92 (7.87)
4j	54.00 (54.16)	3.55 (3.47)	7.52 (7.45)
4k	60.74 (60.63)	4.60 (4.52)	7.79 (7.87)
4l	61.23 (61.51)	5.05 (4.97)	7.65 (7.54)
4m	49.70 (49.64)	3.50 (3.47)	6.40 (6.45)
4n	53.72 (53.85)	3.85 (3.76)	10.61 (10.46)
5a	48.78 (48.90)	3.30 (3.37)	13.65 (13.45)
5b	50.00 (50.09)	3.85 (3.73)	13.15 (13.02)
5c	44.99 (45.17)	2.91 (2.89)	12.31 (12.43)
5d	53.16 (53.31)	4.17 (4.05)	14.12 (13.95)
5e	51.43 (51.21)	4.15 (4.07)	12.74 (12.61)
5f	42.12 (42.35)	2.98 (2.96)	10.89 (11.00)
5g	45.49 (45.38)	3.25 (3.17)	14.54 (14.70)
5h	55.17 (55.09)	3.85 (3.80)	15.00 (15.16)
5i	56.10 (56.20)	4.35 (4.19)	14.50 (14.60)
5j	50.52 (50.40)	3.40 (3.32)	13.72 (13.87)
5k	56.60 (56.36)	4.33 (4.22)	14.78 (14.64)
5l	57.00 (57.24)	4.72 (4.55)	14.21 (14.09)
5m	46.74 (46.64)	3.37 (3.26)	12.02 (12.12)
5n	50.45 (50.34)	3.60 (3.52)	16.50 (16.30)
6a	72.20 (72.31)	5.08 (4.99)	– –
6b	72.79 (72.94)	5.34 (5.44)	– –
6c	64.52 (64.45)	4.17 (4.13)	– –
6d	73.22 (72.94)	5.30 (5.44)	– –
6e	73.73 (73.51)	5.69 (5.84)	– –
6f	57.42 (57.60)	3.96 (4.02)	– –
6g	63.08 (63.32)	4.64 (4.46)	– –

EXPERIMENTAL SECTION

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by thin layer chromatography [silica gel-G, 60-120 mesh, BDH); hexane: ethyl acetate (3:1) as eluent]. The IR spectra were recorded on a Perkin-Elmer Grating Infrared spectrophotometer (ν_{max} in cm^{-1}) model 337 in KBr pellets. The ^1H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 using a Bruker Spectrospin (90 MHz) or Varian EM-360 (200 MHz) Spectrometers with TMS as an internal standard (chemical shifts in ppm). The microanalytical data were obtained from University of Poona, Pune, India. Following are the general procedures for the preparation of various compounds.

Semicarbazone of Phenacyl E-Styryl Sulfone (2). General Procedure.- A mixture of phenacyl E-styryl sulfone[1] **1** (1 g, 0.0033 mol), semicarbazide hydrochloride (0.369 g, 0.0033 mol) and sodium acetate (0.800 g) in ethanol (50 mL) was refluxed for 3-4 hours on the steam bath. The contents were cooled and poured onto crushed ice. The product obtained was filtered and washed with water, dried and recrystallized from ethanol to obtain pure **2**.

4-Aryl-5-styrylsulfonyl-1,2,3-selenadiazole (3). General Procedure.- Semicarbazone **2** (0.500 g, 0.0014 mol) was treated with selenium dioxide powder (0.154 g, 0.0014 mol) in glacial acetic acid (50 mL) and the mixture was gently heated with stirring until the evolution of gas ceased. After completion of the reaction, the mixture was filtered. The filtrate was poured onto crushed ice and the solid which separated was washed thoroughly with cold water and sodium bicarbonate solution. The resultant product was purified by column chromatography to get pure **3**.

4-Aryl-5-styrylsulfonyl-1,2,3-thiadiazole (3). General Procedure.- Semicarbazone **2** (0.400 g, 0.0011 mol) was added portionwise to an excess of thionyl chloride (4 mL) at ice-bath temperature and kept 1 hour at room temperature. Methylene chloride (15 mL) was added and the reaction mixture was decomposed with ice-cold saturated sodium carbonate solution. The organic layer was thoroughly washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave crude product which was purified by column chromatography to afford pure **3**.

4-Aryl-5-(2'-arylcyclopropylsulfonyl)-1,2,3-selena/thiadiazole (4). General Procedure.- A mixture of 4-aryl-5-styryl sulfonyl-1,2,3-selena/thiadiazole **3** (0.411 g / 0.360 g, 0.001 mol) and trimethylsulfoxonium iodide (0.242 g, 0.0011 mol) in 25 mL of methylene chloride was taken. The contents were stirred with 25 mL of 50% aqueous sodium hydroxide until a clear two-phase system was obtained. Then, 100 mg of benzyltriethyl ammonium chloride (BTEAC) was added and stirring continued for a further period of 2-3 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, 100 mL of water was added. The organic layer was separated, washed with water, brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a syrupy substance which solidified on treatment with 2-propanol. The crude product was recrystallized from 2-propanol to obtain pure **4**.

4-Aryl-5-(4'-aryl-3'-sulfonyl-2'-pyrazolyl)-1,2,3-selena/thiadiazole (5). General Procedure.- To a solution of 4-aryl-5-styrylsulfonyl-1,2,3-selena or thiadiazole **3** (0.411 g / 0.360 g, 0.001 mol) in chlo-

roform at 0° was added an ethereal solution of diazomethane (40 mL, 0.2 M) and triethylamine (0.06 g). The reaction mixture was kept at -20° to -15° for 48 h. The solvent was then removed using a rotary evaporator at room temperature to give a product which was subjected to column chromatography to get pure **5**.

2-Arylethynyl-2-arylcyclopropyl Sulfone (6). General Procedure.- To a solution of 4-aryl-5-(2'-arylcyclopropylsulfonyl)-1,2,3-selenadiazole/4-aryl-5-(4'-aryl-3'-sulfonyl-2'-pyrazolyl)-1,2,3-selenadiazole (**4a-g/5a-g**) (2 g) in dichloromethane was added copper powder (15g/30 g). The solvent was removed in such a way that the solid material covered the walls of the flask. The flask was immersed in an oil bath heated to 200° and the pyrolysis was carried out under a nitrogen atmosphere. The pyrolysate was dissolved in CCl_4 and chromatographed on silica gel to get pure **6**.

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