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Note

Phenacyl aryl sulfones as synthons for 1,2,3-selenadiazoles and thiadiazoles

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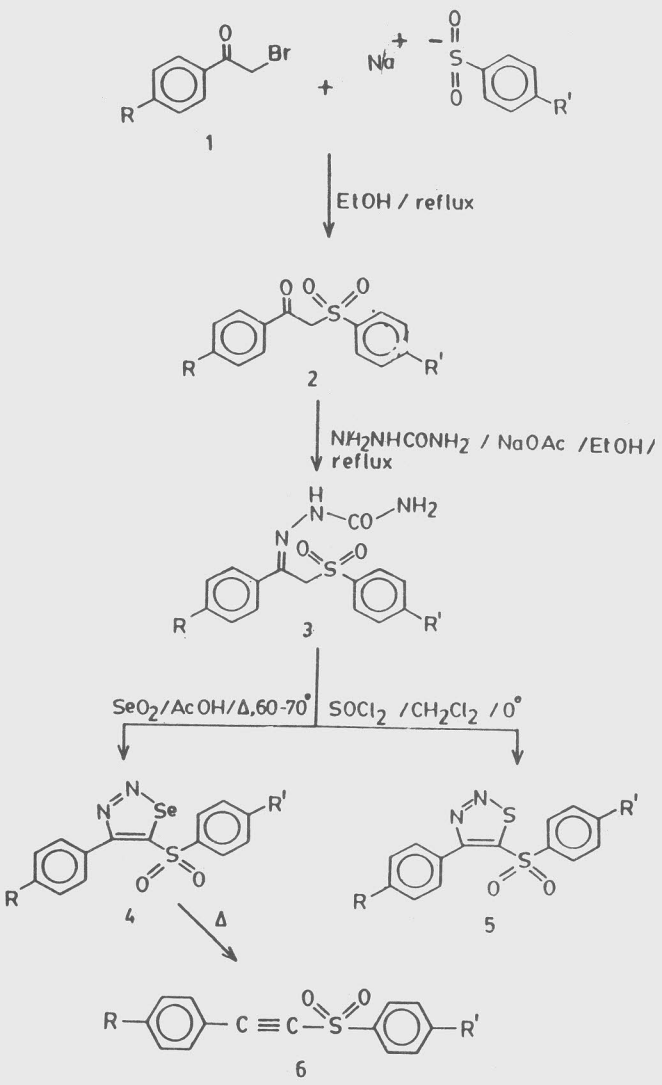
4-Aryl-5-arylsulfonyl-1,2,3-selenadiazole **4a-l** and 4-aryl-5-arylsulfonyl-1,2,3-thiadiazole **5a-l** have been prepared from phenacyl aryl sulfones (**2a-l**). The **4** on pyrolysis yields 1-arylsulfonyl-2-aryl acetylenes **6a-l**.

In our recent communications[1,2] we have reported the synthesis of some selena- and thiadiazoles from cyclohexanone dicarboxylates and 4-piperidones. We have now extended our work to synthesize 4-aryl-5-arylsulfonyl-1,2,3-selenadiazoles and a new class of 1,2,3-selenadiazoles/thiadiazoles from the simple analogues of phenacyl bromides. In fact, the latter have been utilized as key intermediates to build up various heterocycles viz., thiomorpholines[3,4], pyrazolines[5] etc. A number of sulfur containing heterocycles are known to be biologically active. Since, sulfur and selenium being isosteric and also their toxicities do not differ much, it was considered that the synthesis of 1,2,3-selena/thiadiazoles would be of importance[6]. The latter could be obtained by the selenium dioxide oxidation/thionyl chloride treatment of aldehyde or ketone semicarbazones having α-methyl or methylene group[7,8]. In view of the above, the α-methylene ketones, phenacyl aryl sulfones derived from phenacyl bromides have been utilized as synthons to synthesize hitherto unknown selena/thiadiazoles.

The synthetic method involves the condensation of phenacyl bromides **1** prepared from appropriate aetophenones, with sodium aryl sulfinates to get phenacyl aryl sulfones[9] **2**. **2** on reaction with semicarbazide hydrochloride followed by cyclization with selenium dioxide yields 1,2,3-selenadiazole **4**. On the other hand phenacyl arylsulfonyl semicarbazone **3** on treatment with thionyl chloride affords thiadiazoles **5**. The reactivity of **4** has been assessed by pyrolysis leading to the formation of 1-arylsulfonyl-2-arylacetylenes **6** (Scheme I). However, **5** seems to be thermally quite stable under similar conditions[10]. Thus, this forms yet another convenient route for the synthesis of sulfonyl acetylenes[11].



Scheme I

IR spectra of **3** displayed absorption bands in the regions 3420 and 3340 cm^{-1} indicating the presence of NHCO and $CONH_2$ groups[12] respectively. The compounds **4** and **5** exhibited bands at 1485

and 645 cm^{-1} due to N=N and C-S/Se groups, respectively. All the compounds showed bands around 1360 and 1140 cm^{-1} due to asymmetric and symmetric vibrations of SO_2 group[3].

^{1}HNMR spectra (δ, ppm) of **3** showed two sharp signals at 5.20 and 7.72 for CH_2 and NH_2 protons, respectively. The NH signal of semicarbazone moiety is merged with aromatic protons. The signals due to NH and NH_2 disappeared on deuteration. On the other hand, compounds **4, 5** and **6** exhibited multiplets in the region 6.75-7.45 due to aromatic protons. The absence of a singlet at 5.2 in **4** and **5** clearly indicates that the active methylene group present in 3 is involved in building up of the selena-and thiadiazole rings. The mass spectrum of **4a, 5a** and **6a** exhibited low intense molecular ion peaks at m/z 349, 302 and 242, respectively. Expulsion of nitrogen is observed in **4a** and **5a** resulting ions at m/z 321 and 274, respectively. 1-Phenylsulfonyl-2-phenylacetylene radical cation (m/z 242) is commonly observed in both the cases, **4a** and **5a**. All the compounds exhibited peaks at m/z 178, 101 and 77 due to 1,2-diphenylacetylene radical cation, phenylacetylene and phenyl cations, respectively. The latter ion appeared as the basic peak in all the cases.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. The purity of the compounds was checked by chromatography over silica gel thin layers [Silica gel-G, hexane: ethyl acetate (3:1) as eluants]. IR spectra were recorded in KBr pellets using a Perkin-Elmer 993 infrared spectrometer (ν_{max} in cm^{-1}); ^{1}H NMR spectra in $CDCl_3$ using 90 MHz Perkin-Elmer instrument with TMS as an internal standard (chemical shifts in δ, ppm); and mass spectra on Jeol JMS-D 300 instrument at 70 eV. Microanalytical data were obtained from Central Electrochemical Research Institution, Karaikudi, India.

Preparation of phenacyl aryl sulfonyl semicarbazone 3a-l. A mixture of phenacyl aryl sulfone[5] **2** (1g, 0.039 mole), semicarbazide hydrochloride (0.434 g, 0.039 mole) and sodium acetate (0.530 g, 0.039 mole) in ethanol (40 mL) was refluxed for 3-5 hr on a steam-bath and cooled. The separated solid was filtered, washed with water and recrystallized from ethanol to get **3**. Physical data of **3a-l** are given in Table I.

4-Aryl-5-arylsulfonyl-1,2,3-selenadiazole 4a-l

Semicarbazone **3** (0.59 g 0.001 mole) was treated with selenium dioxide powder (0.111 g,

Table I—Physical data of compounds **3-6**

Compd	R	R'	Yield (%)	m.p. (0°C)	Mol.. formula (Mol. wt)	Found (%) (Calcd) C	H	N
3a	H	H	65	182-84	$C_{15}H_{15}N_3O_3S$ (317.37)	56.62 (56.77	4.79 4.77	13.17 13.25)
3b	H	CH_3	75	196-98	$C_{16}H_{16}N_3O_3S$ (330.38)	58.24 (58.17	4.96 4.89	12.79 12.72)
3c	H	Cl	63	194-96	$C_{15}H_{14}N_3O_3SCl$ (351.81)	51.32 (51.22	4.11 4.02	11.74 11.95)
3d	CH_3	H	74	190-92	—	—	—	—
3e	CH_3	CH_3	63	216-18	$C_{17}H_{19}NO_3S$ (345.42)	59.24 (59.12	6.60 5.55	12.30 12.16)
3f	Cl	H	66	210-12	—	—	—	—
3g	Cl	Cl	60	224-26	—	—	—	—
3h	Br	CH_3	69	216-18	$C_{16}H_{16}N_3O_3SBr$ (410.29)	46.77 (46.84	3.15 3.93	10.46 10.25)
3i	Br	Cl	68	226-28	$C_{15}H_{13}N_3O_3SClBr$ (430.71)	41.74 (41.83	3.10 3.05	9.84 9.76)
3j	NO_2	H	75	202-04	$C_{15}H_{14}N_4O_5S$ (362.36)	49.85 (49.72	3.82 3.89	15.38 15.47)
3k	OC_2H_5	H	75	198-200	$C_{17}H_{19}N_3O_4S$ (361.42)	56.68 (56.56	5.34 5.30	11.52 11.63)

Contd.

Table I—Physical data of compounds **3-6**—*Contd*

Compd	R	R'	Yield (%)	m.p. (0°C)	Mol. formula (Mol. wt)	Found (%) (Calcd) C	H	N
3l	OC_2H_5	CH_3	76	188-90	$C_{18}H_{21}N_3O_4S$ (375.44)	57.44 (57.59	5.59 5.64	11.27 11.19)
4a	H	H	62	140-42	$C_{14}H_{10}N_2O_2SSe$ (349.27)	48.24 (48.15	2.92 2.89	8.09 8.02)
4b	H	CH_3	65	138-40	$C_{15}H_{12}N_2OSSe$ (363..302)	49.49 (49.60	3.38 3.32	7.83 7.71)
4c	H	Cl	65	150-52	—	—	—	—
4d	CH_3	H	63	146-48	—	—	—	—
4e	CH_3	H	66	160-62	—	—	—	—
4f	Cl	H	60	154-56	$C_{14}H_9N_2O_2SSeCl$ (384.228)	43.86 (43.77	2.40 2.36	7.21 7.30)
4g	Cl	Cl	62	158-60	—	—	—	—
4h	Br	CH_3	64	152-54	—	—	—	—
4i	Br	Cl	62	158-60	$C_{14}H_8N_2O_2SSeClBr$ (462.83)	36.48 (36.34	1.83 1.75	6.23 6.09)
4j	NO_2	H	65	148-50	$C_{14}H_9N_3O_4SSe$ (394.27)	42.74 (42.65	2.35 2.30	10.49 10.65)
4k	OC_2H_5	H	72	136-38	—	—	—	—
4l	OC_2H_5	CH_3	70	148-50	—	—	—	—
5a	H	H	79	110-12	$C_{14}H_{10}N_2O_2S_2$ (30.27)	55.69 (55.62	3.28 3.34	9.22 9.27)
5b	H	CH_3	78	106-08	—	—	—	—
5c	H	Cl	76	106-08	$C_{14}H_9N_2O_2SCl$ (336.82)	50.01 (49.93	2.65 2.69	8.41 8.32)
5d	CH_3	H	76	96-98	—	—	—	—
5e	CH_3	CH_3	72	102-04	—	—	—	—
5f	Cl	H	78	106-08	—	—	—	—
5g	Cl	Cl	76	150-52	—	—	—	—
5h	Br	CH_3	70	100-02	$C_{15}H_{11}N_2O_2S_2Br$ (395.30)	45.69 (45.58	2.77 2.80	7.20 7.08)
5i	Br	Cl	77	108-10	—	—	—	—
5j	NO_2	H	79	102-04	—	—	—	—
5k	OC_2H_5	H	80	154-56	$C_{16}H_{14}N_2O_3S_2$ (346.42)	55.36 (55.48	4.12 4.07	7.99 8.08)
6a	H	H	62	85-86	$C_{14}H_{10}O_2S$ (242.29)	69.53 (69.40	4.22 4.16	— —)
6b	H	CH_3	65	92-93	—	—	—	—
6c	H	Cl	70	86-88	$C_{14}H_9O_2SCl$ (226.74)	60.61 (60.77	3.24 3.28	— —)
6d	CH_3	H	61	95-96	—	—	—	—
6e	CH_3	CH_3	66	100-101	$C_{16}H_{14}O_2S$ (270.35)	71.21 (71.08	5.31 5.22	— —)
6f	Cl	H	72	94-95	—	—	—	—
6g	Cl	Cl	69	105-06	—	—	—	—
6h	Br	CH_3	64	109-11	—	—	—	—
6i	Br	Cl	72	115-16	$C_{14}H_8O_2SClBr$ (335.64)	47.38 (47.29	2.25 2.27	— —)
6j	NO_2	H	64	120-21	—	—	—	—
6k	OC_2H_5	H	58	89-90	$C_{16}H_{14}O_3S$ (286.35)	67.27 (67.12	4.98 4.93	— —)
6l	OC_2H_5	CH_3	62	96-97	$C_{17}H_{16}O_3S$ (300.37)	68.12 (67.98	5.45 5.37	— —)

0.001 mol) in gl. acetic acid (20 mL) and the mixture was gently heated (50-60°) with stirring until the evolution of gas ceased. The reaction mixture was cooled and then poured onto crushed ice. The solid obtained was filtered, dried and recrystallized from pet. ether (60-80°C) to afford the pure product **4**. The physical data of **4a-l** are given in Table I.

4-Aryl-5-arylsulfonyl-1,2,3-thiadiazole 5a-l. Semicarbazone **3** (0.500 g, 0.001 mole) was added portionwise to the thionyl chloride (1.5 mL) at 0-5°C and kept at room temperature for 1-2 hr. Dichloromethane (10 mL) was added to the reaction mixture and decomposed with an ice cold sodium carbonate solution. The organic layer was washed with water (4-5 times each with 10 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent a gummy substance was obtained, which was solidified on treatment with cyclohexane and purified by recrystallization from ethanol to get the pure product **5**.The physical data of **5a-l** are given in Table I.

1-Arylsulfonyl-2-arylacetylenes 6a-l. The appropriate selenadiazole (**4**) (0.01 mole) was heated for 10-15 min. above its melting point. The resultant solid was purified by column chromatography using silica gel (60-120 mesh, BDH) with ethyl acetate-hexane (1:3) as eluants. The physical data of **6a-l** are given in Table I.

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