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Note

Synthesis of newer selenadiazoles and thiadiazoles from their chroman-4-one precursors

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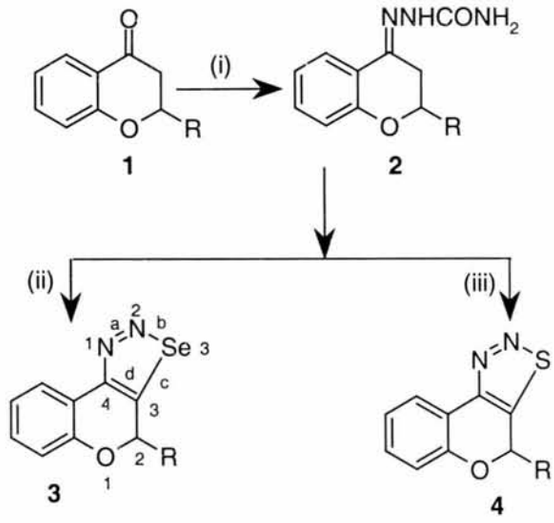
A newer series of 13 compounds viz. 2-aryl-3,4-dihydrobenzopyrano [3, 4-*d*]-1, 2, 3-selenadiazoles **3** and 2-aryl-3,4-*d*ihydrobenzopyrano [3,4-*d*]-1, 2, 3-thiadiazoles **4** have been synthesized from their chroman-4-one precursors.

Substituted chroman-4-ones, a class of oxygen heterocycles are common among the natural products and are extensively used as synthetic intermediates [1]. They have been used to prepare various fused heterocyclic ring systems and have been used for a wide range of pharmacological activity[2]. Some chroman-4-ones with medical use are khellin, a coronary vasodilator[3,4], chroman-4-one-2-carboxylic acids, a spasmolytic agent and disodium chromoglycate, and an antiallergenic drug [5].

On the other hand, it is well known that a number of heterocyclic compounds containing nitrogen and sulfur exhibit a wide variety of biological activities. However, reports about selenium containing heterocycles are relatively less[6-8], although some of them are used as chemotherapeutic agents[9]; also some 1, 3, 4 - and 1, 2, 3- selena/thiadiazoles were found to possess significant antibacterial and antiviral activities[7,10].

The fused ring systems of chroman-4-ones are found to posses enhanced biological activities and the synthesis of the title heterocycles (selenadiazoles and thiadiazoles) is of growing interest, say, 1,2,3-selena/thiadiazole rings, worked out by Bhaskar Reddy *et al.*[11-19] fused to carbocyclic/heterocyclic rings. Therefore, as a part of continuation of our work[20] on chromone nucleus, it was thought to synthesize 1,2,3-selena/thiadiazoles fused to chroman-4-ones.

A series of such compounds as 2-aryl-3,4-dihydrobenzopyrano [3, 4-*d*]-1,2,3-selenadiazoles **3** and 2-aryl-3,4-dihydrobenzopyrano [3, 4-*d*]-1, 2, 3-thiadiazoles **4** have been synthesized (**Scheme I**). The carbonyl function in **1** (chroman-4-ones) has been exploited for the synthesis of selenadiazoles **3** and thiadiazloles **4**. Chroman-4-ones **1** on condensation with semicarbazide hydrochloride gave its semicarbazones **2** which on SeO_2 oxidation afforded **3**.



(i) = NaOAc, $NH_2CONHNH_2$ HCl, reflux
(ii) = AcOH, SeO_2, 60 °C
(iii) = $SOCl_2$, -10 to 0 °C, CH_2Cl_2, $NaHCO_3$

Scheme I

On the other hand, **2** on treatment with thionyl chloride at -10 to 0°C yielded **4**. The formation of the compounds **3** and **4** was confirmed as there were no characteristics absorptions at 3400 cm^{-1} (NH) and 3200cm^{-1} (NH_2) and on the other hand the characteristic absorption bands for compounds **3** and **4** were observed at 1475 and 1487 (N=N), 700 (N-S-C), 685 (C-Se-N), 700 cm^{-1}(C-S-N), respectively. Also ^{1}H NMR spectra for compounds **3** and **4** gave added confirmation for their formation as the spectra displayed peaks at δ 7.0-8.2 (8H, Ar-H) and at 6.6(s, O-C-H).

Experimental Section

Melting points were taken in open capillaries in paraffin oil-bath and are uncorrected. The purity of the compounds was checked on TLC. IR spectra were recorded in nujol on a Perkin- Elmer 337 spectrophotometer (λ max in cm^{-1}); and ^{1}H NMR spectra on a Varian Gemini 200 MHz spectrometer using TMS as internal standard (chemical shifts in δ, ppm).

2-(4-Chlorophenyl)-3,4-dihydrobenzopyrano [3, 4-*d*]-1, 2, 3-selenadiazoles 3b. Compound **2** (R= *p*-Cl,

1.5 g, 0.005mole) was dissolved in 15-20 mL of acetic acid, warmed the solution in oil-bath to 60°C. To this was added SeO_2 (0.55g, 0.005 mole) portionwise with constant stirring maintaining the temperature at 60°C. After the complete transfer of SeO_2 the reaction mixture was stirred for 3 hr maintaining the same temperature. The mixture was then cooled to room temperature, and poured on crushed ice, and digested for 30 min. The precipitate thus obtained was filtered, dried and purified by column chromatography to give the product **3b**; yield 84%, m.p. 128°C; (**Table I**) IR (Nujol): 1475(N=N), 1220(C-O-C), 680(C-Se-N) cm^{-1}; ^1H NMR (200MHz, $CDCl_3$): δ 7.2-8.2(m, 8H, Ar-H), 6.6(s, 1H, O-C-H); Mass: (M^+- 348), (M^{+2}-350), m/z 319 (98% aban.), 285(100% base peak), 205(45%), 176(75%); ^{13}C NMR: δ 78.41(C-2), 116.78 (C-9), 117.85(C-8), 122.81(C-6), 124.94(C-7), 127.96(C-5), 129.06(C-1'), 130.35(C-2', C-6'), 135.20(C-3', C-5'), 138.40(C-4'), 151.89(C-3), 153.50(C-4), 159.46(C-10). **3d:** ^1H NMR: δ 6.8-7.5(m, Ar-H, 8H), 6.5(s, O-C-H, 1H), 2.5(s, 3H, CH_3). **3e:** ^1H NMR: δ 7.5-8.2(m, 8H, Ar-H), 6.8(s, 1H, O-C-H).

2-(4-Chlorophenyl)-3,4-dihydrobenzopyrano [3,4-*d*]-1,2,3-thiadiazoles 4b. Redistilled thionyl chloride (5 mL) was taken in clean, dry 50 mL round bottom flask kept in a salt ice-bath and the temperature allowed to fall down up to -10°C. To it was added with constant magnetic stirring 1.578 g of compound **2b** (R=*p*-Cl, 0.005 mole) in portions maintaining the temperature below 0°C. After the complete addition,

Table I—Characterization data of compounds **3a-m** and **4a-m**

Compd	R	m.p.	Yield	Found (%) (Calcd)			Compd	R	m.p.	Yield	Found (%) (Calcd)		
		(°C)	(%)	C	H	N			(°C)	(%)	C	H	N
3a	C_6H_5	148	68	57.48	3.17	8.93	**4a**	C_6H_5	182	78	67.64	3.72	10.49
				(57.51	3.19	8.94)					(67.66	3.75	10.52)
3b	*p*-Cl- C_6H_4	128	84	51.78	2.56	8.02	**4b**	*p*-Cl- C_6H_4	115	85	59.87	2.96	9.30
				(51.80	2.59	8.05)					(59.90	2.99	9.31)
3c	*p*-MeO-C_6H_4	173	69	55.96	3.45	8.15	**4c**	*p*-MeO-C_6H_4	108	64	64.83	4.03	9.51
				(55.98	3.49	8.16)					(64.86	4.05	9.54)
3d	*p*-Me-C_6H_4	205	78	58.69	3.65	8.53	**4d**	*p*-Me-C_6H_4	162	72	68.56	4.25	9.98
				(58.72	3.67	8.56)					(68.57	4.28	10.00)
3e	*p*-NO_2-C_6H_4	98	66	58.26	2.48	11.70	**4e**	*p*-NO_2-C_6H_4	178	80	57.85	2.88	13.47
				(58.28	2.51	11.73)					(57.87	2.89	13.50)
3f	*o*-OH- C_6H_4	131	63	54.69	3.00	8.49	**4f**	*o*-OH-C_6H_4	118	60	63.79	3.51	9.90
				(54.71	3.03	8.51)					(63.82	3.54	9.92)
3g	*o*-Cl-C_6H_4	78	71	51.77	2.57	8.04	**4g**	*o*-Cl-C_6H_4	171	80	59.87	2.97	9.28
				(51.80	2.59	8.05)					(59.90	2.99	9.31)
3h	*m*-Cl-C_6H_4	100	60	51.79	2.56	8.02	**4h**	*m*-Cl-C_6H_4	148	69	59.88	2.96	9.29
				(51.80	2.59	8.05)					(59.90	2.99	9.31)
3i	$(MeO)_3$ C_6H_2	184	81	53.57	3.95	6.7	**4i**	$(MeO)_3$ C_6H_2	98	82	60.64	4.46	7.84
				(53.60	3.97	6.9)					(60.67	4.49	7.86)
3j	Cinnamyl	112	77	57.48	3.18	8.92	**4j**	Cinnamyl	130	73	67.63	3.72	10.49
				(57.51	3.19	8.94)					(67.66	3.75	10.52)
3k	Furyl	139	65	51.46	2.61	8.21	**4k**	Furyl		81	60.92	3.09	10.90
				(51.49	2.64	8.24)					(60.93	3.12	10.93)
3l	*o*-Me C_6H_4	104	70	58.70	3.64	8.55	**4l**	*o*-Me-C_6H_4	120	76	68.54	4.25	9.98
				(58.72	3.67	8.56)					(68.57	4.28	10.00)
3m	*m*-Me-C_6H_4	176	58	58.69	3.65	8.52	**4m**	*m*-Me-C_6H_4	138	70	68.56	4.26	9.97
											(68.57	4.28	10.00)

Solvent for crystallization: Ethanol

temperature was allowed to rise to room temperature and 30 mL of dichloromethane was added. The mixture was stirred for further 1 hr. Excess thionyl chloride was decomposed using saturated $NaHCO_3$ solution and the product **4b** isolated using extractive isolation technique. Further purification was achieved by column chromatography, yield 86 %, mp 115°C (**Table I**); IR (Nujol): 1487(N=N), 1230(C-O-C), 700 (C-S-N) cm^{-1}; ^1H NMR (200MHz, $CDCl_3$): δ 7.0-8.2 (m, 8H, ArH), 6.7(s, 1H, O-C-H); Mass: (M^+-300), M^{+2}-302, m/z 271(100% base peak), 237(95%), 228(10%), 208(20%), 165(15%) etc.

4d: ^1H NMR: δ 7.0-7.5(m, Ar-H, 8H), 6.2(s, O-C-H, 1H), 2.6(s, CH_3 group, 3H). **4e:** ^1H NMR: δ 7.5-8.4(m, Ar-H, 8H), 6.7(s, O-C-H, 1H).

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