Asian Journal of Chemistry Vol. 12, No. 2 (2000), 501–505

Synthesis of Benzopyranopyrazoles

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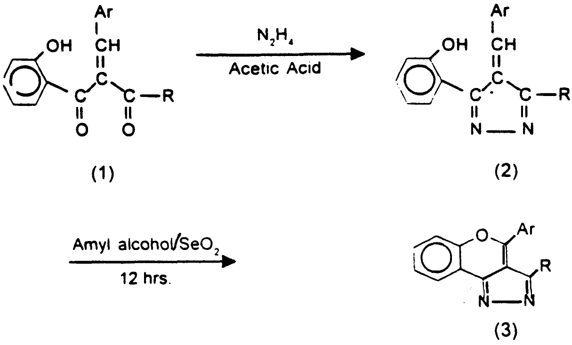
3-Aryl-4-arylidine-5-(*o*-hydroxyphenyl)-pyrazoles (2) and 2,7-diaryl-4H-1-(3,4-c)-benzopyranopyrazoles (3) are obtained by the condensation of 2′-hydroxy-2-aroyl-3-aryl-acrylophenones and hydrazine hydrate and oxidative cyclization of (2) with selenium dioxide respectively. Their structures have been supported on the basis of elemental analysis and spectral data.

INTRODUCTION

The 4H-1-benzopyran nucleus which is a major part of 4H-1 benzopyrone (chromone) and flavone (2-phenyl chromone) plays an important role for various biological activities.[1, 2] Certain alkyl and aryl pyrazole derivatives have shown quite significant bacteriostatic, bacteriocidal and fungicidal properties.[3, 4] Alkyl and aryl pyrazoles themselves have a sharply pronounced sedative action on the central nervous system. These observations prompted us to synthesise some condensed ring compounds possessing both benzopyran and pyrazole nuclei. In this work, we report the synthesis of several fused benzopyranopyrazoles (3) utilising 3-aryl-4-arylidine-5-(*o*-hydroxyphenyl)-pyrazoles (2) as a starting compounds.

The method is an oxidative cyclization of 3-aryl-4-arylidine-5-(*o*-hydroxyphenyl)-pyrazoles (2) with selenium dioxide in boiling amyl alcohol leading to the formation of 2,7-diaryl-4H-1 (3, 4-c)-benzopyranopyrazoles (3). Its alcoholic solution did not change the colour of $FeCl_3$. The required pyrazoles were synthesised by refluxing appropriate arylophenone and hydrazine hydrate in acetic acid[5].



EXPERIMENTAL

Melting points were taken in open capillaries and are uncorrected. The IR spectra (KBr) were recorded on a Perkin-Elmer Model 283 B and PMR on Varian FT -80A, 200 MHz spectrometer.

The required *o*-hydroxydiaroyl methane was prepared following an earlier known procedure.[6,7] The 2′-hydroxy-2-aroyl-3-aryl-acrylophenone (1) was prepared by the interaction of *o*-hydroxydiaroyl methane and different aldehydes in boiling ethanol in the presence of a few drops of piperidine.

3-(4-Chlorophenyl)-4-benzylidine-5-(*o*-hydroxy phenyl)-pyrazole (2)

A mixture of 2′-hydroxy-2-(4-chlorobenzoyl)-3-phenyl acrylophenone (0.002 mol) and hydrazine hydrate (15%, 5 mL) was refluxed in acetic acid for 1 h. It was then allowed to cool and diluted with distilled water, and the solid obtained was crystallised from ethanol. Yield *ca.* 30%.

IR (λ_{max}): 3350 cm^{-1} ν(OH), 1600 cm^{-1} ν(C=N), 1480 cm^{-1} ν(C=C).

NMR: δ 2.34 (S, 3H—Ar—CH_3), 6.84–7.58 (m, 10H, Ar—H, NH=CH) and 10.82 (S, 1H—OH)

All other compounds of this series were prepared by following the same procedure and their analytical data are recorded in Table-1.

TABLE-1
PHYSICAL DATA OF COMPOUND (2)

Compound No.	Ar	Yield (%)	m.p. (°C)	m.f.	% Nitrogen	
					Found	Calcd.
	R = phenyl					
1.	*p*-CH_3-C_6H_4	60	229	$C_{23}H_{18}ON_2$	8.40	8.24
2.	*m*-NO_2-C_6H_4	70	201	$C_{22}H_{15}O_3N_3$	11.24	11.38
	R = o-Chlorophenyl					
3.	C_6H_5	69	130	$C_{22}H_{15}ON_2Cl$	7.02	7.82
4.	*m*-Cl-C_6H_4	50	191	$C_{22}H_{15}ON_2Cl_3$	7.00	7.14
5.	*m*-NO_2-C_6H_4	51	209	$C_{22}H_{14}O_3N_3Cl$	10.21	10.40
6.	2-Furyl	58	180	$C_{20}H_{13}O_2N_2Cl$	7.92	8.04
7.	*o*-Cl-C_6H_4	52	140	$C_{22}H_{14}ON_2Cl_2$	7.01	7.14
8.	*p*-Cl-C_6H_4	55	150	$C_{22}H_{14}ON_2Cl_2$	7.02	7.14
	R = p-Chloro phenyl					
9.	C_6H_5	55	240	$C_{22}H_{15}ON_2Cl$	7.51	7.82
10.	*o*-Cl-C_6H_4	50	186	$C_{22}H_{14}ON_2Cl_2$	6.98	7.14
11.	*m*-NO_2-C_6H_4	55	202	$C_{22}H_{14}O_3N_3Cl_2$	10.17	10.40
12.	2-pyridyl	60	196	$C_{21}H_{14}ON_3Cl$	11.52	11.69
13.	4-Pyridyl	55	181	$C_{21}H_{14}ON_3Cl$	11.57	11.69
14.	2-Furyl	50	140	$C_{20}H_{13}O_2N_2Cl$	7.89	8.04
15.	*p*-Cl-C_6H_4	52	178	$C_{22}H_{14}ON_2Cl_2$	7.94	7.14
16.	*p*-OCH_3-C_6H_4	67	243	$C_{23}H_{17}O_2N_2Cl$	7.01	7.21

Compound No.	Ar	Yield (%)	m.p. (°C)	m.f.	% Nitrogen	
					Found	Calcd.
	R = 2-furyl					
17.	C_6H_4	50	181	$C_{20}H_{14}O_2N_2$	8.79	8.91
18.	*p*-Cl-C_6H_4	58	178	$C_{20}H_{15}O_2N_2Cl$	7.89	8.04
19.	*p*-OCH_3-C_6H_4	45	183	$C_{21}H_{16}O_3N_2$	8.04	8.13
20.	*o*-Cl-C_6H_4	40	150	$C_{20}H_{13}O_2N_2Cl$	7.87	8.04
21.	*m*-NO_2-C_6H_4	46	163	$C_{20}H_{13}O_4N_3$	11.42	11.69
22.	*o*-Cl-C_6H_4	72	160	$C_{20}H_{13}O_2N_2Cl$	7.88	8.04
23.	3-Pyridyl	70	184	$C_{19}H_{13}O_2N_3$	13.08	13.30
24.	*p*-Br-C_6H_4	66	195	$C_{20}H_{13}O_2N_2Br$	7.01	7.12
	R = 3-pyridyl					
25.	C_6H_5	60	188	$C_{21}H_{15}ON_3$	12.78	12.92
26.	*p*-OCH_3-C_6H_4	79	110	$C_{22}H_{17}O_2N_2$	11.49	11.83
27.	*m*-Cl-C_6H_4	78	190	$C_{22}H_{14}ON_3Cl$	11.42	11.69
28.	*o*-Cl-C_6H_4	80	136	$C_{21}H_{14}ON_3Cl$	11.39	11.69
29.	*o*-Br-C_6H_4	66	120	$C_{21}H_{14}ON_3Br$	10.32	10.42
30.	*m*-OCH_3-C_6H_4	60	161	$C_{22}H_{17}O_2N_3$	11.54	11.83
31.	*o*-NO_2-C_6H_4	70	171	$C_{21}H_{14}O_3N_4$	15.04	15.13
	R = *p*-CH_3-phenyl					
32.	C_6H_4	58	179	$C_{23}H_{18}ON_2$	8.01	8.20
33.	3, 4-$(OCH_3)_2$-C_6H_3	60	167	$C_{25}H_{23}O_3N_2$	6.98	7.01
34.	*o*-Cl-C_6H_5	67	90	$C_{23}H_{17}ON_2Cl$	7.32	7.52
35.	2-furyl	68	187	$C_{21}H_{16}O_2N_2$	8.38	8.53
36.	*p*-Cl-C_6H_4	61	139	$C_{23}H_{17}ON_2Cl$	7.35	7.52

*Satisfactory C, H analyses were obtained for all the compounds.

2-Phenyl-7-(4-chlorophenyl)-4H-1 (3,4-c)-benzopyranopyrazole: (3)

A mixture of isoamyl alcohol (25 mL), 3-(4-chlorophenyl)-4-benzylidine-5-(o-hydroxy phenyl)-pyrazole (0.01 mol.) and selenium dioxide (0.03 mol.) was refluxed for 12 h. The reaction mixture was cooled, filtered and then subjected to steam distillation to remove isoamyl alcohol. The non-steam volatile residue was washed with dilute sodium carbonate solution and water was evaporated to dryness. The solid mass thus obtained was crystallised from alcohol in colourless needles. Yield 60%.

IR (λ_{max}): 1600 cm^{-1} $\nu(C{=}N)$, 1070 cm^{-1} $\nu(C{-}O{-}C)$, 985 cm^{-1} (pyrazole ring).

NMR: δ 6.8–7.9 (m, 13H, Ar—H).

The I.R. spectra of 2-phenyl-7-(4-chorophenyl)-4H-1(3,4-c)-benzopyranopyrazole (3) shows no peak due to —OH group thereby suggesting that (2) has undergone oxidative ring closure to give the benzopyropyrazole (3).

Similarly, all other compounds of this series were prepared by following the same procedure and their analytical data are recorded in Table-2.

TABLE-2
PHYSICAL DATA OF COMPOUND (3)

Compounds No.	Ar	Yield (%)	m.p. (°C)	m.f.	% Nitrogen	
					Found	Calcd.
	R = phenyl					
1.	C_6H_5	55	200	$C_{22}H_{14}ON_2$	8.50	8.69
2.	*o*-Cl-C_6H_5	51	140	$C_{22}H_{13}ON_2Cl$	7.69	7.86
3.	*p*-CH_3-C_6H_5	55	219	$C_{23}H_{16}ON_2$	8.27	8.33
4.	3-Pyridyl	55	145	$C_{21}H_{13}ON_3$	13.31	13.56
5.	*p*-OCH_3-C_6H_4	60	218	$C_{23}H_{16}O_2N_2$	7.80	7.91
6.	*m*-NO_2-C_6H_4	50	160	$C_{22}H_{13}O_3N_3$	11.37	11.44
	R = *o*-chlorophenyl					
7.	C_6H_5	40	184	$C_{22}H_{13}ON_2Cl$	7.77	7.86
8.	*m*-Cl-C_6H_4	50	128	$C_{22}H_{12}ON_2Cl_2$	7.05	7.17
9.	*m*-NO_2-C_6H_4	51	182	$C_{22}H_{12}O_3N_3Cl$	10.30	10.40
10.	2-Pyridyl	55	144	$C_{21}H_{12}ON_3Cl$	11.59	11.76
11.	2-Furyl	54	115	$C_{20}H_{11}O_2N_2Cl$	8.04	8.09
12.	*o*-Cl-C_6H_4	48	132	$C_{22}H_{12}ON_2Cl_2$	7.02	7.17
	R = p-chlorophenyl					
13.	C_6H_5	60	218	$C_{22}H_{13}ON_2Cl$	7.69	7.80
14.	*o*-Cl-C_6H_4	50	160	$C_{22}H_{12}ON_2Cl_2$	7.05	7.19
15.	*m*-NO_2-C_6H_4	60	251	$C_{22}H_{13}O_3N_3Cl$	10.27	10.40
16.	2-Pyridyl	60	220	$C_{21}H_{12}ON_3Cl$	11.67	11.76
17.	4-Pyridyl	70	212	$C_{21}H_{12}ON_3Cl$	11.72	11.76
18.	2-Furyl	69	130	$C_{20}H_{11}O_2N_2Cl$	8.00	8.09
19.	*p*-Cl-C_6H_4	60	221	$C_{22}H_{12}ON_2Cl_2$	7.01	7.17
20.	*p*-CH_3-C_6H_4	50	170	$C_{23}H_{15}ON_2Cl$	7.37	7.56
	R = 2-furyl					
21.	C_6H_5	50	179	$C_{20}H_{12}O_2N_2$	8.70	8.90
22.	*p*-Cl-C_6H_4	55	175	$C_{20}H_{11}O_2N_3Cl$	8.00	8.09
23.	*p*-OCH_3-C_6H_4	45	178	$C_{21}H_{14}O_3N_2$	8.01	8.18
24.	*m*-Cl-C_6H_4	49	150	$C_{20}H_{11}O_2N_2Cl$	7.94	8.09
25.	*m*-NO_2-C_6H_4	60	119	$C_{20}H_{11}O_4N_3$	11.52	11.76
26.	o-Cl-C_6H_4	59	141	$C_{20}H_{11}O_2N_3Cl$	8.02	8.09
27.	3-Pyridyl	55	121	$C_{19}H_{11}O_2N_3$	13.25	13.41
	R = 3-Pyridyl					
28.	*o*-Cl-C_6H_4	50	105	$C_{21}H_{12}ON_3Cl$	11.57	11.70
29	*p*-OCH_3-C_6H_4	60	160	$C_{22}H_{15}O_2N_3$	11.65	11.80
30	3-Cl-C_6H_4	55	110	$C_{21}H_{12}ON_3Cl$	11.57	11.70

*Statisfactory C, H analyses were obtained for all the compound.

ACKNOWLEDGEMENTS

The authors thank the Director, CDRI, Lucknow for spectral and elemental analysis. One of the authors (RMK) is also thankful to P.T. Kosankar, Department of Chemistry, Nagpur University, Nagpur for his encouragement.

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(*Received*: 26 October 1999; *Accepted:* 10 December 1999) AJC-1937