International Journal of Recent Research and Review, Vol. XI, Issue 4, December 2018
ISSN 2277 – 8322

Synthesis and Characterization of Some New Schiff Bases Containing Coumarin Moiety

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Abstract **- Some new Schiff bases coumarin containing coumarine was synthesized by knovena gel reaction then when bromination of this compound resulted in 3-(2-bromoacyl) coumarine (2),while the treatment of compound (2) with thiourea to give thiazol derivatives (3). Schiff base (4a- k) were also prepared by treating of thiazol compound (3) with different aldehydes. The synthesized compounds were characterized on the bases of their physical properties and spectroscopic data.**

Keywords **- Schiff base, thiazole, coumarine, Acetyl coumarin.**

I. INTRODUCTION

Imines group (–C=N–) containing compounds typically known as Schiff bases have been synthesized by the condensation of primary amines with active carbonyls.in medicinal and pharmaceutical chemistry with several biological applications that include antifungal [1] antibacterial [2] antiflamatry [3] analgesic[4], antifungal [5]and antimicrobial activity[6]. Also, Schiff base play a vital role in polymers [7] and printer ink [8]. Similarly, coumarin derivatives have been of good interest because of their role in natural and synthetic organic chemistry. Many products which contain a coumarin exhibit biological activity such as molluscicides [9] anthelmintic, hypnotic, insecticidal [10]activity and some are serving as anticoagulant agents[11]It is well established that the biological activity associated with the hydrazone compounds attributed to the presence of the active imine group. Hence, many Schiff base compounds containing this active moiety showed good anticancer bioactivities according to the literature [12].

II. EXPERIMENTAL SETUP

Melting points were determined on an electro thermal 9300 melting point apparatus and are uncorrected. IR spectra were recorded on a Bruker optics (FT-IR) spectrophotometer Co. using KBr-disk. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 300-MHzspectrometer using TMS as an internal standard and DMSO-d_6 as a solvent. UV spectra were delivered by Shimadzu UV-Visible recording UV-160 spectrophotometer.

A. Preparation 3-acetyl-2H-chromen-2-one (1)[13]

salicylaldehyde (1.22 g, 0.01 mole) was added to ethyl aceto acetate(1.3 g,0.01 mole) ,the mixture was cooled to (10˚C), then (1 ml) of piperidine was added. The reaction mixture was stirred at room temperature until the solid was appeared, the resulting solid was filtered, dried and recrystallized from aqueous ethanol to give the corresponding compound (1) as a crystal pale yellow (90%) (m.p. 121-123˚C)**.**

B.Preparation of 3-(2-bromoacetyl)-2H-chromen-2-one (2)[14]

To a solution of compound (1) (4.7g, 0.025mole) in (25ml) chloroform,(4g,1.3ml)bromine in (5ml)of chloroform were added gradually, then reflux the mixture for about one hour cooled in an ice-water with stirring, the precipitated product was filtered off, and washed with ether, dried to give a crystal yellow(72%) (m.p. 166-168˚C)**.**

C.Preparation of 3-(2-aminothiazol-4-yl)-2H-chromen-2-one (3) [15]

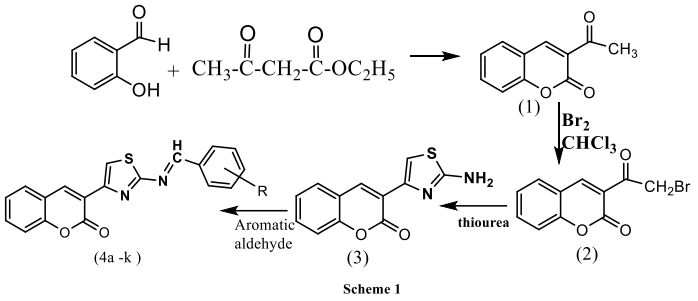
Dissolved(5.3g,0.02mole)of compound (2) in (20ml) of ethanol ,then (1.52g,0.02mole)of thiourea was added and refluxed for an hour ,then (5ml) of pyridine was added for further one hour The reaction mixture was cooled in an ice-water with stirring, the precipitated product was filtered off, and washed with ether, dried to give a crystal yellow (65%) (m.p. 230-233˚C)**.**

D. Preparation of 3-(2-(substituted benzylidene amino)thiazol-4-yl)-2H-chromen-2-one (4) [16]

(0.005 mole)from suitable aromatic aldehydes were added to a solution of (1.2g,0.005mole)of compound(3) in(20ml) absolute ethanol ,then little drops of glacial acetic acid was added. The reaction mixture were reflux for (24hours)and reduced this solution to a half amount ,cool andthe resulting solid was filtered and washed with cold ethanol several times dried to give a solid product and recrystallized from suitable solvent. The physical data are listed in (Tables I) for the corresponding compounds (4a-k).

III. RESULTS AND DISSCUSION

Schiff bases were found to be an important structural unite to construct a large number of organic compounds through their various reactions with different organic reagents. Salicylal dehydetreated with ethyl acetoacetate in the presence of piperidine at (10^oC) yielded 3-acetyl-2H-chromen-2-one(1). Treating compound(1**)** in chloroform with bromine in chloroform yielded3-(2-bromoacetyl)-2H-chromen-2-one(2)**,** on treatment of compound (2)with thiourea gave 3-(2-aminothiazol-4-yl)-2H-chromen-2-one (3).Finally 3-(2-(substituted benzylidene amino)thiazol-4-yl)-2H-chromen-2-one (4a-k)were achieved by reaction of 3-(2-aminothiazol-4-yl)-2H-chromen-2-one(3)with different aromatic aldehydes as shown in (Scheme 1).



Scheme 1

The IR spectra for compounds (4a-k) showed the following stretching bands; (1580-1635cm^{-1}) due to the (C=N) bond for heterocyclic ring, (1630-1670cm^{-1})due to (C=N) bond for Schiff base as shown in tableII.

The ^{1}H-NMR spectra for compounds (4a,4c,4e and 4h)in (DMSO-d_6) which showed multiple bands due to aromatic parts ,also single bands in the range (8.83-8,97ppm) due to (N=CH group) in these compounds, in addition the singlet peaks in the range(8.9 -8.14ppm) for proton of (CH of chromone)and singlet peak sin the range (8,23-8,41ppm) due to proton for CH of thiazole. While the (CH_2 group for thiazole ring showed as doublet bands in the range (4,19-4.24ppm),in addition other group in these compounds as shown in tableIII.

^{13}C-NMR Spectra showed peaks for compounds(4a,4c,4e and 4h) showed peaks of carbon for structures which gave additional support to the results as shown in tableIII..

IV. REFERENCES

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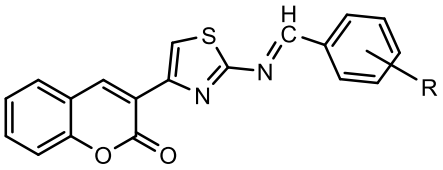
TABLE I

Physical data for compounds (4a-k)



Comp. No.	**R**	**m.p °C**	**Yield %**	**Color**	**Cryst. solvent**
4a	4-Cl	120-122	48	pale yellow	EtOH
4b	2-OH	195-197	59	pale yellow	EtOH+ H_2O
4c	2,5-di-OH	190-193	55	brown	MeOH
4d	2,3-di-OH	210-212	57	light brown	EtOH
4e	4-OMe	133-135	75	dark brown	EtOH
4f	2,6-di-Cl	199-201	45	light brown	MeOH
4g	2-Cl	193-195	80	pale yellow	EtOH+ H_2O
4h	3-NO_2	211-213	73	pale yellow	MeOH
4i	2,4-di-OH	185-188	66	brown	EtOH+ H_2O
4j	2,4-di-OMe	178-180	68	brown	EtOH
4k	2-NO_2	135-137	50	pale yellow	MeOH

TABLE II

Spectral data for compounds (4a-K)

Compd. No.	R	UV ($CHCl_3$) λ_{max} nm	IR (KBr),υcm^{-1}		
			C=N thiazol	C=N Schiff bases	OH
4a	4-Cl	291	1605	1630	---
4b	2-OH	346	1620	1660	3450
4c	2,5-di-OH	357	1600	1650	3280
4d	2,3-di-OH	361	1610	1640	3400
4e	4-OMe	289	1615	1635	
4f	2,6-di-Cl	281	1635	1635	
4g	2-Cl	282	1610	1670	
4h	3-NO_2	257	1610	1660	
4i	2,4-di-OH	340	1590	1640	3400
4j	2,4-diOMe	301	1580	1635	
4k	2-NO_2	262	1610	1640	

Table III

^{1}H-NMRand ^{13}C-NMR data for compounds (4a,4c.4e and 4h)

Compd. No.	^{1}H-NMR (δ,ppm)	^{13}C-NMR (δ,ppm)
4a	δ 8.13 (bs, 1H,CHcoumarine ring). δ 8.34(s, 1H, CH thiazolering). δ 8.83(bs, 1H,N=CH). δ 4.22(d, 2H,CH_2).δ 7,36-7.88(m, 8H-ArH.)	42.68,116.23,120.5,124.5,125.11 127.3,128.2,130.11,134.22,149,11,153.22 160.22,161.21
4c	δ 8.09(bs, 1H,CH coumarine ring). δ 8.23(s, 1H, CH thiazolering). δ 8.91(bs,1H,N=CH),4.19(d,2H,CH_2). δ 7,31-7.76(m, 8H-ArH.), δ 11,2(bs, 1H,OH)	43.12,116.34,120.43,124.24,125.32 127.22,128.6,130.54,134.76,149,09,153.15 160.1,161.45,171,23,196.11
4e	δ 3,82(s, 3H,OMe,)δ 8.14(bs, 1H,CH coumarinering).δ 8.41(s, 1H, CH thiazole ring).δ 8.96(bs, 1H,CH). δ 4.24(d,2H,CH_2).δ 7,07-7.88(m, 8H-ArH.),	43.52,116.22,120.76,124.55,125.11 127.45,128.55,130.44,134.22,149,12,153.44 160.21,161.4,171,23,
4h	δ 8.14(bs, 1H,CHcoumarine ring). δ 8.31(s, 1H, CH thiazolering). δ 8.97(bs, 1H,CH). δ 4.22(d,2H,CH_2). δ 7,23-8,02(m, 8H-ArH.),	43.22,116.05,120.33,124.87,125.12 127.33,128.43,130.45,134.01,149,44,153.08 160.33,161.55,171,22.