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Synthesis, Characterization of some New 4-Thiazolidinone of Acenaphthoquinone

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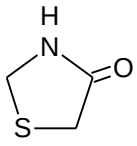
***Abstract*— This work summarized with Synthesis of schiff's bases 1(a-c) from reaction of parent compound acenaphthoquinon with primary amines . Treating of imines compounds with thioglycolic acid was produced thiazolidinone derivatives 2 (a-c) .The structures of synthesized compounds were confirmed by using some spectroscopic analysis such as FT.IR , 1H-NMR and 13C-NMR spectral**

***Keywords*— thioglycolic acid ; 13C-NMR spectra ; Acenaphthenquinone; thiazolidin**

I. INTRODUCTION

Thiazolidined-4-one are the derivatives of thiazolidine which belong to an important group of heterocyclic compounds containing sulfur and nitrogen in a five member ring [(1)] 1,3-Thiazolidin-4-ones are heterocyclic at position 1 containing a sulfur atom , position 3 nitrogen and position 4 carbonyl group[(2)] figure (1) .Thiazolidine and its composites are key components of many natural products and drugs . In addition, Thiazolidine found to uses as antitubercular [(3)], antibacterial [(4)], anti-inflammatory [(5)] , as antiviral agents, especially as anti-HIV agents [(6)], anticancer [(7,8)], anticonvulsant [(9)] and antidiabetic activity [(10)].



Figure(1): Thiazolidinone ring

II. EXPERIMENTAL PART

A. *General procedure for the preparation of imines 1(a-c)*

In general[(11)], imines prepared by mixed the amine with acenaphthoquinone in (25 ml) of Suitable solvent ethanol and add (10 -15) drops of glacial acetic acid were refluxed in water bath for (24 – 25) h .The reaction was followed up with TLC the eluent using [Hexane :Ethyl acetate (7:3)]. When the reaction completion the solvent removed by evaporation then the product recrystallized by methanol.

B. *(1Z,2E)-N,N'-bis(4-methylphenyl)-2a,5-dihydroacenaphthylene-1,2-diimine(1a)*

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with 4-methylaniline (1.176 g , 10.978 mmol) m.p = 220-222 R_f = 0.9 IR (KBr disk):(1629. 85) cm^{-1} (C=N) yield = 78% .

C. *(1Z,2E)-N,N'-bis(4-(dimethylamino) phenyl)-2a,5-dihydro acenaphthylene-1,2-diimine (1b)*

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with N,N-dimethylbenzene-1,4-diamine (1.495 g , 10.978 mmol) m.p = 246-248 R_f = 0.7 IR (KBr disk): (C=N) 1654. 92 cm^{-1} yield = 76 % .

D. *(2Z)-2-[(4-bromophenyl)imino]-6,8a-dihydroacenaphthylen -1(2H)-one ((1c)*

Prepared by reaction Acenaphthenquinone (1g, 5.489 mmol) with 4- bromoaniline (0.94g , 5.489 mmol) m.p = 238-240 R_f = 0.8 IR (KBr disk): 1654. 92cm^{-1} (C=N) yield = 72 % .

E. *General Procedure of thiazoledinones 2(a-c)*

In general, [(12)] the thiazoledinones were mixed with imines 1(a-c) and thioglycolic acid in (15 ml) chloroform , Then refluxed for (18-24) h with Stirring. The reaction monitord by TLC using eluent [n-Hexane-Ethyl acetate (3:7)] . When The reaction completed the solvent removed to give thiazoledinone. The product was precipitated and recrystallized with the addition of methanol droplets.

F. *N-(4-methylphenyl)-4'-spiro[acenaphthylene-2,2'-thiazolidine] (2a)*

Prepared by reacting (1g, 2.778 mmole) (2*E*)-2-[(4-methylphenyl) imino]-1,2-diphenyl ethanone (1a) and (0.674mL, 0,.447g, 5. 556 mmole) of thioglycolic acid. R_f = 0.7 , yield = 63 %, m.p. =232-234 °C. IR (KBr disk): 1689.64 cm-1 (–N–C=O).

G. N-(4--(dimethylamino) phenyl)-4'-spiro[acenaphthylene-2,2'-thiazolidine] (2b)

Prepared by reacting (1g, 3.049 mmole) (1*Z*,2*E*)-*N*, *N*'-bis (4-(dimethylamino) phenyl)-2a,5-dihydroacenaphthylene-1,2-diimine(1b) and (0.354 mL, 0,.469 g, 6. 098 mmole) of thioglycolic acid. R_f = 0.7 , yield = 60%, m.p. = 255-257°C. IR (KBr disk): 1686.51cm-1 (–N–C=O)

H. N-(4-bromophenyl)-4'-spiro[acenaphthylene-2-thiazolidine] (2c)

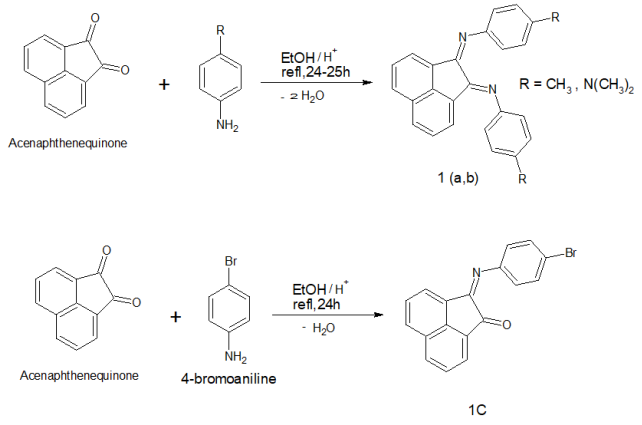
prepared by reacting (1g, 2.974 mmole) (2Z)-2-[(4-bromophenyl)imino]-6,8a-dihydroacenaphthylen -1(2H)-one (1c) and (0.361 mL, 0.272 g, 2.974 mmole) of thioglycolic acid R_f = 0.8 , yield = 62 %, m.p. = 236-238 °C. IR (KBr disk): 1698.85 cm-1 (–N–C=O)

III. MEASUREMENTS

Melting points were determined in open capillary tubes using an electro thermal melting point /SMP3I apparatus. FTIR spectra in the range (200-4000) cm^{-1} were recorded as KBr discs using a Shimadzu FTIR spectrophotometer,The. ^{1}H-NMR were recorded on VARIAN spectrophotometer (300 MHz), the ^{13}C-NMR spectra were recorded using VARIAN spectrophotometer (75 MHz) relative to the internal standard tetramethylsilane (TMS) , DMSO-d_6 used as solvent.

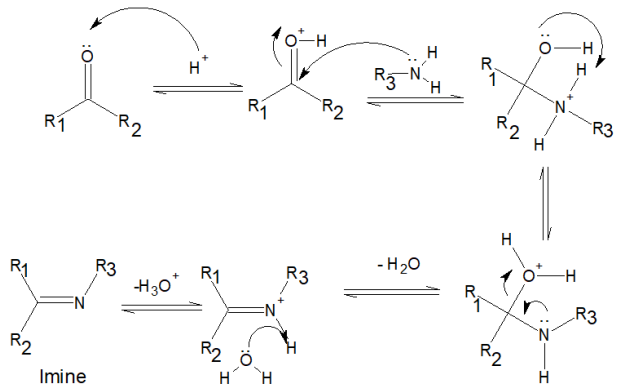
IV. RESULT AND DISCUSSION

Prepared Compounds1(a-c) from the reaction of acenaphthoquinone with 4-methylaniline , N,N-dimethylbenzene-1,4-diamine and 4-bromoaniline respectively with the presence of glacial acetic acid in absolute ethanol as shown in scheme (1) .



scheme (1): Synthesis of the compounds 1(a–c)

The reaction involves a nucleophilic attack of the amine group on the carbon of the carbonyl group of the ketone to form a compound N-(substituted hemiaminals) which loses a water molecule to give the stable compound . Mechanism of imines formation [13] shown in scheme (2)



scheme(2): Mechanism of imines formation

Measured the melting points Compounds 1(a-c) as show in Table (1) diagnosed by specifying (FT-IR) shown in Table (2). It features ranges corresponding to the expansion vibrations , azomethine band (C=N) ,aromatic (C=C) ,bands aromatic (C-H) and aliphatic (C-H) . These bands occur (1629.85, 1654.92,1654.92) , (1587.42, 1602.85, 1598.99),(3051.39, 3047.53 ,3055.24),(2916.37,-----, 2835.36) cm^{-1} respectively .

Table (1) shows the physical properties data imines 1(a-c)

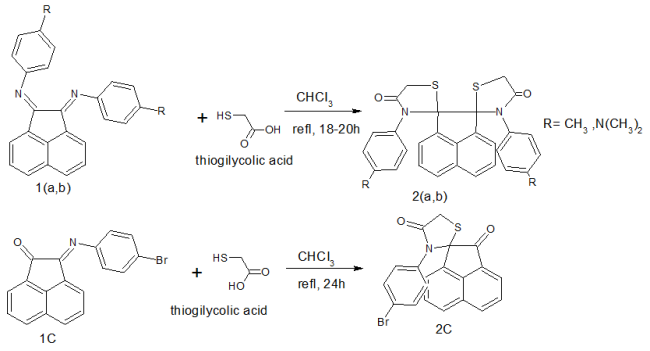
Comp. 1 (a-c)	m.p.°C	Colour	Reaction time
1 a	220-222	Orange	24h
1b	246-248	Red	25h
1c	238-240	Yellow	24h

Table (2): shows IR spectra of Imines 1(a-c)

Comp. 1(a-c)	Aromatic C-H stretching cm^{-1}	Aliphatic C-H stretching cm^{-1}	Azomethine C=N stretching cm^{-1}	Aromatic C=C stretching cm^{-1}
1 a	3051.39	2916.37	1629.85	1587.42
1b	3047.53	2875.86	1654.92	1602.85
1c	3055.24	2972.31	1654.92	1598.99

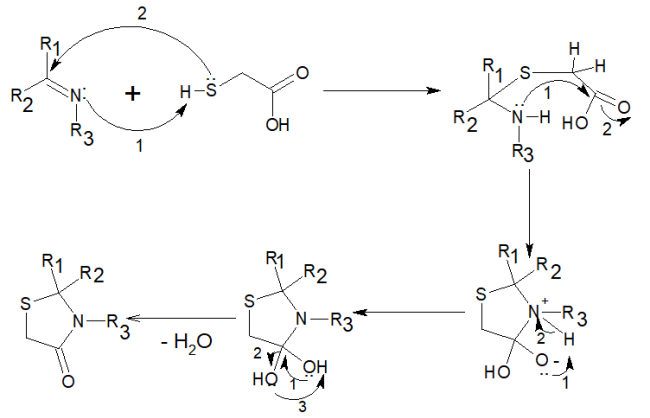
V. SYNTHESIS 4-THIAZOLDINON

Compounds were 2(a-c) prepared from the reaction of imines 1(a-c) with acid thioglycolic acid in absolute chloroform as shown in scheme (3) .



Scheme (3): Synthesis of the compounds 2(a–c)

Involved mechanism cycloaddition[13] formation 4-Thiazoldinone as shown in Scheme (4)



scheme (4) Mechanism of 4-Thiazoldinone formation

The melting point of the prepared compounds 2(a-c) was measured as shown in Table (3) The (FTIR) spectra Table (4) of compound 2(a-c) show featured packages most notably, C-H aromatic, aromatic C=C , aliphatic C-H andcarbonyl amide group which occur within;- (3051.39, 3054.83, 3069.35),(1608.63, 1606.28, 1691.57),(2920.23, 2984.09, 1600.77),(1689.64, 1686.51, 1600.77)

Table 3: physical properties of thiazoledinones 2(a-c)

Comp. 2 (a-c)	m.p.°C	Colour	Reaction time
2 a	232-234	Grey	24h
2b	255-257	Yellow	25h
2c	236-238	White	24h

Table (4): FTIR spectral data of Thiazolidinones 2(a-c)

Comp. 2 (a-c)	**Aromatic C-H stretching cm^{-1}**	**Aromatic C=C stretching cm^{-1}**	**Aliphatic C-H stretching cm^{-1}**	**Amide C=O stretching cm^{-1} (thia-)**
2 a	3051.39	1608.63	2920.23	1689.64
2b	3054.83	1606.28	2984.09	1686.51
2c	3069.35	1691.57	1600.77	1698.58

The ^{1}H-NMR of 2(a-c) shows signals at δ(2.39) ppm for CH_3 Component (2a) and δ(2.51) ppm for N-$(CH_3)_2$ Component (2b) also show characteristic chemical shift (CH_2) group of thiazoledinone ring showed doublet of doublet signal at chemical shift δ [dd-(4.10- 4.05ppm, *J* =15HZ) - (4.08- 4.03ppm, *J* =15HZ) - (4.12- 4.07ppm, *J* =15HZ)],and doublet of doublet signal at chemical shift δ [dd-(4.34- 4.29ppm,*J* =15HZ) - (4.23- 4.18ppm, *J* =15HZ) - (4.27- 4.22ppm, *J* =15HZ) respectively . a multiplet signal at δ (6.72-8.01) ,(6.39-8.29),(6.89-8.28) ppm for aromatic protons respectively as show Table (5) .

^{13}C-NMR spectral of 2(a-c) gives signal at δ(20.89) ppm for carbon -CH_3 Component (2a) , at δ(40.11) ppm for carbon –NCH_3 Component (2b) and characteristic signal of 2(a-c) of thiazoledinone ring show at[(33.17) , (32.92), (33.07) ppm] for carbon –CH_2- , at[(72.98) , (73.55), (73.29) ppm] for carbon S-C-N ,at[(172.67) , (172.55), (172.41) ppm] for carbon –N-C=O as show Table (6) .

Table(5): ^{1}H-NMR spectral data of Thiazolidinones 2(a-c)

Comp. 2 (a-c)	**thiazolidin-4-one ring**		**Aromatic proton**	**Aliphatic proton**
	C -H ring , *J* Hz	**C -H ring , *J*Hz**		
2 a	4.10-4.05 ppm *J* =15HZ	4.34-4.29ppm *J* =15HZ	6.72-8.01	2.39
2b	4.08-4.03 ppm *J* =15HZ	4.23-4.18ppm *J* =15HZ	6.39-8.29	2.51
2c	4.12-4.07ppm *J* =15HZ	4.27-4.22ppm *J* =15HZ	6.89-8.28	----

Table(6) ^{13}C-NMR spectral data of Thiazolidinones2(a-c)

	Chemical shift ppm				
Comp. 2 (a-c)	**-CH2-**	**C-N-S**	**N-C=O**	**C-Ar**	**Other**
2 a	33.17	72.98	172.67	118.08 - 148.24	-(CH_3) 20.89
2b	32.92	73.55	172.55	112.37-150.05	------
2c	33.07	73.29	172.42	121.72-140.58	-(NCH) 40.11

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