Synthesis and Characterization of Heterocyclic Compounds Derived From 4- Hydroxy and 4-Amino Acetophenone

Nisreen H. Karam
Jumbad H. Tomma
Ammar H. AL-dujaili
Dept. of Chemistry /College of Education For Pure Science (Ibn Al- Haitham)/ University of Baghdad

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Abstract

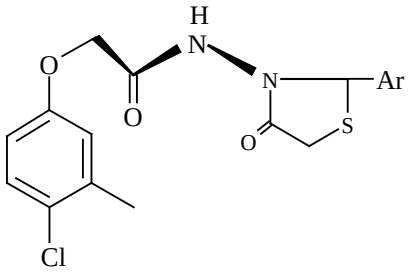
Two series of Schiff Bases $[VI]_n$ and thiazolidin-4-one derivatives$[VII]_n$ were synthesized by many steps starting from cyclization of 4- hydroxyacetophenon with thiourea in iodine to yield 1,3-thiazole compound which was reacted with pentoxy bromide in anhydrous potassium carbonate to converted compound[II] and this reacted with Phenol to yield azo compound[III]. The azo compound reacted with ethyl chloro acetate in basic medium to get a new easter compound[IV] which is converted to their acid hydrazid[V]. The later compound condensation with n-alkoxy benzaldehyde to give new Schiff bases$[VI]_n$. Imine group undergoes addition cyclization with thioglycolic acid to get thiazolidinone compounds$[VII]_n$ .Also, two new series of Schiff Bases $[XII]_n$ and their thiazolidin-4-one derivatives$[XIII]_n$ were synthesized by using the same steps given for synthesis Schiff bases [VI]n and thiazoidinone [VII]n except using 4- aminoacetophenon instead of 4-hydroxyacetophenon(see scheme 2) .The synthesized compounds were characterized by melting points , FTIR ,C.H.N.S analysis , ^{1}HNMR and Mass spectroscopy (of some of them) .

Keywords: Thiazole, thiazolidinone, heterocyclic compounds , Schiff bases

Introduction

The thiazolidin-4-one ring have reported to a wide range of pharmacologic activities which include antimicrobial[1] ,antifungal[2], antitumor[3] ,antidiabetic activity [4], anti-inflammatory[5] and stomach toxicity [6]. Over views of their synthesis , properties , reactions and applications have been published [7,8] .

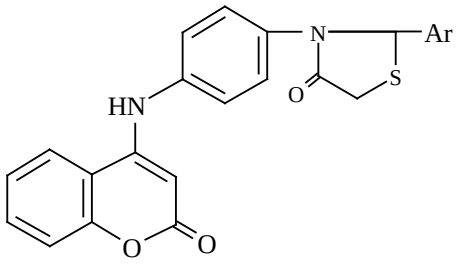
Fuloria et al [9] synthesized 2-(4-chloro-3-methylphenoxy)-N-(4-oxo-2-arylthiazolidin-3-yl) acetamide (1) by Cyclization N-(substituted benzylidiene)-2-(4-chloro-3-methylphenoxy)acetamide with thioglycolic acid in the presence of zinc chloride.



Ar=C_6H_5, 4-ClC_6H_4, 4-HOC_6H_4 or 4-$(CH_3)_2NC_6H_4$

(1)

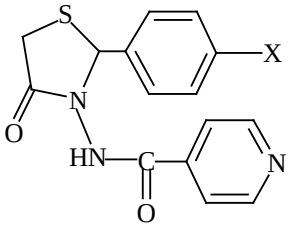
While, Patel et al[10] synthesized a series of novel thiazolidinones(2) by reaction of various Schiff bases of coumarin with thioglycolic acid in dry benzene.



Ar=C_6H_5, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-ClC_6H_4 or 4-$CH_3C_6H_4$

(2)

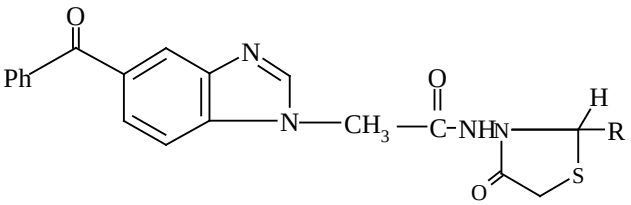
On the other hand, Vinay et al[11] synthesized new derivatives of thiazolidinone(3) by reaction of hydrazone compound with thioglycolic acid in DMF as a solvent.



X=$N(CH_3)_2$ or Cl

(3)

Recently, Kumar et al [12] synthesized new thiazolidinones derivatives 3-(2-(5-benzoyl-1H-benzo[d][1,2,3]imidazol-1-yl)acetyl)-2- alkylthiazolidin-4-one (4) by cyclocondensation of the corresponding Schiff bases compounds with thioglycolic acid in anhydrous $ZnCl_2$



R=C_6H_5, 4-CH_3 C_6H_4, 4-HO-C_6H_4 or 4-CH_3O-C_6H_4

(4)

In this paper , synthesis and characterization of new thiazolidinones derived from new Schiff bases containing another heterocyclic ring(1,3-thiazole).

Experimental

Chemicals

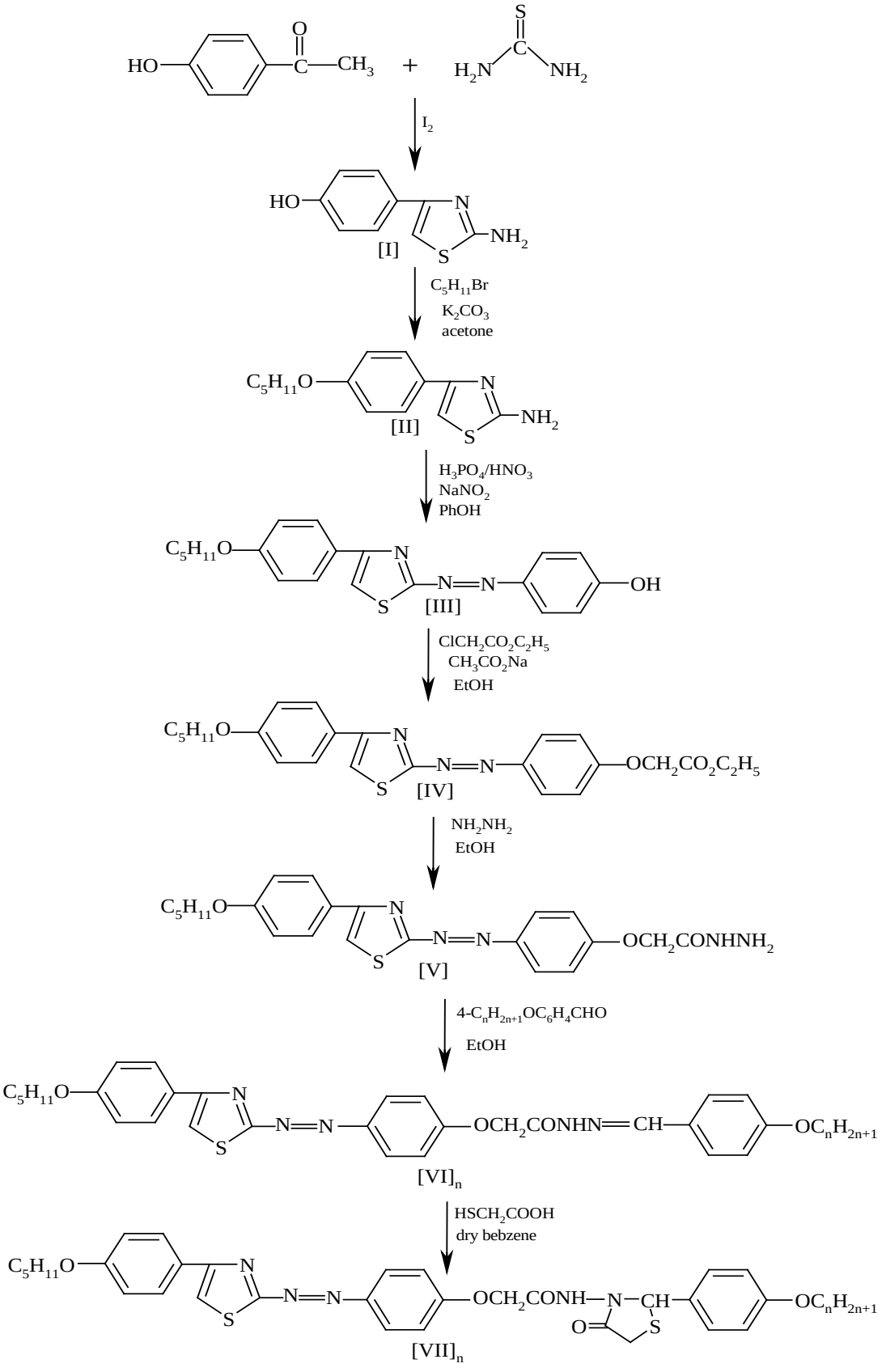
All chemicals were supplied by fluka, merek and Aldrich chemicals Co. and used as received.

Techniques

FTIR spectra were recorded using potassium bromide discs on a Shimadzo(Ir prestige-21) 1HNMR spectra were carried out by company: Bruker , model: ultra-shield 300 MHz , origin : Switzerland and are reported in ppm(δ), DMSO and $CDCl_3$were used as a solvent with TMS as an internal standard,measurements were made at Chemistry Department, Al-albyat University. Elemental micro-analyses of some compounds were performed on a (C.H.N.S) Company: Euro vector, model EA 3000A origin: Italy. University of Al-albayt, Jordan. Mass spectrum were recorded on IEOL JMS-7 high resolution instrument , Jordan. uncorrected melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus.

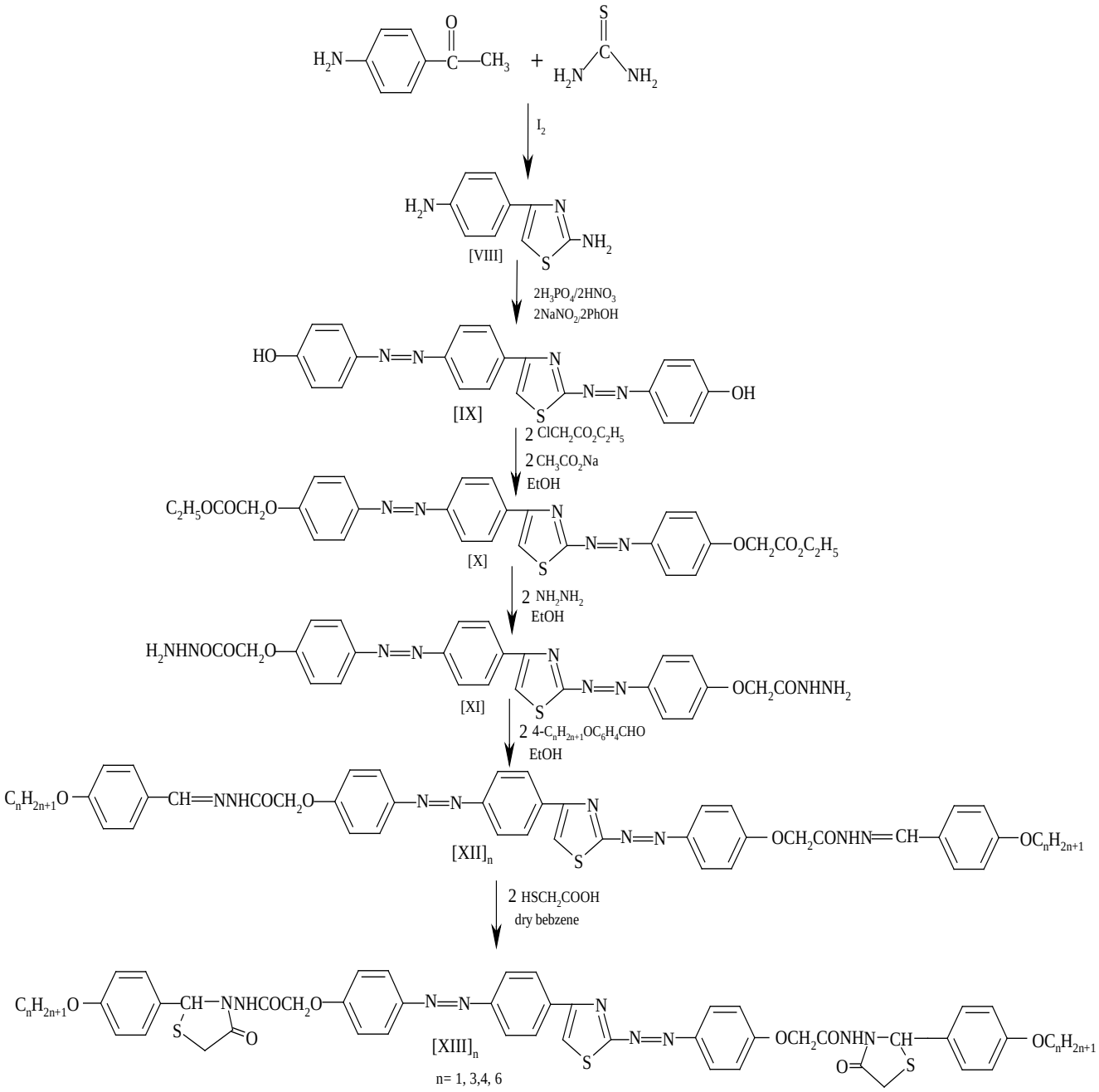
Synthesis

New compounds are synthesized according to scheme1 and scheme2:



n=1,3-8

Scheme1



Scheme2

Synthesis of 4-n-Alkoxybenzaldehyde

Dissolved 4-hydroxybenzaldehyde (10.61g, 0.087 mol) and potassium hydroxide (4.87g, 0.087mol) in 50 mL of absolute ethanol, and added n-alkyl bromide (0.13 mol), the mixture was refluxed for 6 hrs., and potassium bromide was precipitated after that added 50 mL water and 50 mL diethyl ether. The mixture was extracted, and take the organic phase, washed with 25 mL of water and 25 mL of 10% sodium hydroxide solution, then 25 mL of water. Dried the organic phase over magnesium sulphate [13] , then the filtered evaporated to yield 4-alkoxybenzaldehyde yields (75-80%).

Synthesis of 2-Amino 4-(4`-hydroxylphenyl)-1,3-thiazole[I]

In a flask of 250 mL added iodine (7.61g, 0.03mol), thioura (4.56g ,0.006mol) and 4-hydroxyacetophenone (4.08g, 0.003 mol), the mixture was heated for 8 hrs. on the water bath. Cooled, washed by diethyl ether and solution of sodium thiosulfate ,the precipitated was filtered[14]and recrystalized from ethanol .

Yield 89%, m.p= 148-155 ^{o}C

Synthesis of 2-Amino 4-(4`-n- pentoxyphenyl)-1,3-thiazole [II]

A mixture of compound [I] (0.28g ,0.0015mol) and anhydrous potassium carbonate (0.80g, 0.012mol) dissolved in acetone 20 mL ,then n-pentyl bromide (0.004 mol) was added, the mixture was refluxed overnight .Afterward, the mixture was poured into ice water the precipitate was filtered and washed with water,dried and recrystalized from ethanol.

Yield =74% ,m.p= 98-99 ^{o}C

Synthesis of 2-(4`-Hydroxylphenylazo)-4-([4``-n-pentoxy phenyl)-1,3-thiazole [III]

Compound $[II]_5$ (0.44 g, 0.0017 mol) was dissolved by heating and stirring in 8 mL of 85% phosphoric acid. The solution was cooled to 0^{o}C in an ice bath, and then concentrated nitric acid 4 mL and a solution of sodium nitrite (0.10 g, 0.0017mol) in water 2 mL were added. The mixture was stirred vigorously and maintained at below 5^{o}C for10 minutes. Afterwards phenol (0.15g, 0.0017mol) in water 0.5mL was added dropwise with stirring. The brown solid was filtered, washed several times with water, then dissolved in 30mL 10% NaOH, the solution filtered, the crude product precipitated during neutralization with 10%HCl [13], then filtered and washed with water several times , recrystallized from ethanol.Yield 78%, m.p = 60-62 ^{o}C.

Synthesis of 2-(4`-Oxyethylacetate phenylazo)-4-(4``-n-pentoxy phenyl)-1,3-thiazole [IV]

A mixture of compound[III](0.36g,0.001 mol), ethyl α -chloroacetate (0.001 mol) and fused sodium acetate(0.246g,0.003 mol) in ethanol 5 mL was refluxed for 4 hrs. then cooled and poured into cold water . The resulting was filtered and purified by ethanol to give new ester,yield73%, m.p> 295 ^{o}C.

Synthesis of 2-(4`-Oxy acidhydrazide phenylazo)-4-(4``-n-pentoxy phenyl)-1,3- thiazole[V]

A solution of compound [IV] (2.71g,0.006 mol) and hydrazine hydrate 1.5 mL(80%) in absolute ethanol 2.5 mL was heated to reflux during 3 hrs[15]. The mixture was cooled to room temperature, evaporation of solvent and recrystalized from ethanol to yield pale brown compound, yield 80%.

Synthesis of 2-[4`-(4``-Substutiedbenzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxy phenyl)-1,3- thiazole $[VI]_n$

A mixture of compound [V] (0.43g,0.001mol) and different aromatic aldehyde (0.001 mol) dissolved in (15 mL) of absolute ethanol was refluxed for (3-4 hrs.) and cooled to room temperature . The solid product was filtered and recrystallized by ethyl acetate to give new schiff bases.The physical properties are listed in Table1.

Synthesis of Thiazolidin-4-one derivatives$[VII]_n$

A mixture of Schiff bases$[VI]_n$ (0.01mol) and thioglycolic acid (0.01 mol) was refluxed in dry benzene (10 mL) for 12 hrs. The solvent was evaporated and the reaction mixture was neutrilized with sodium bicarbonate solution, the product was filtered off and recrystallized from acetone .The physical properties are listed in Table 2.

Synthesis of 2- Amino 4-(4`-amino phenyl)-1,3-thiazole [VIII]

This compound was synthesized by using the same procedure given for compound [I], except using 4-aminoacetophenone instead of 4-hydroxyacetophenone [14], recrystalized by ethanol.
Yield 83%,m.p= 110-111 ^{o}C.

Synthesis of 2-(4`-Hydroxyphenyl azo)-4-[4``(4```- hydroxy phenyl azo) phenyl]-1,3-thiazole [IX]

This compound was synthesized by using the same procedure given[13] for compound [III], except using the compound[VIII] instead of compound[II], recrystallized from acetone ,color dark brawn ,yield 70%, m.p > 295 ^{o}C.

Synthesis of 2-(4`-Oxyethylacetate phenyl azo)-4-[4``-(4```-oxyethylacetate phenyl azo)] phenyl -1,3-thiazole [X]

This compound was synthesized by using the same procedure given for compound [IV], except using the compound [IX] instead of compound[III] and used (0.002mol),(0.492g ,0.006mol) from ethyl α -chloroacetate , fused sodium acetate respectively . The resulting was filter and purified by ethanol to give brown solid, yield 65%,m.p > 295 ^{o}C.

Synthesis of 2-(4`-Oxy acid hydrazide phenyl azo)-4-[4``-(4```-oxy acid hydrazide phenyl azo)] phenyl -1,3-thiazole [XI]

This compound was synthesized by using the same procedure given[15] for compound [V], except using the compound[X] instead of compound[IV] and used 3mL instead of 1.5 mL hydrazine hydrate. Recrystallized from dichloromethane to yield brown product 82%, m.p= 109-111 ^{o}C.

Synthesis of 2-[4`-(4``- Substutied benzaledine amino)-oxy acetamide] phenyl azo-4-[4```-(4````- substutied benzaledineamino)-oxy acetamide phenyl azo] phenyl -1,3-thiazole $[XII]_n$

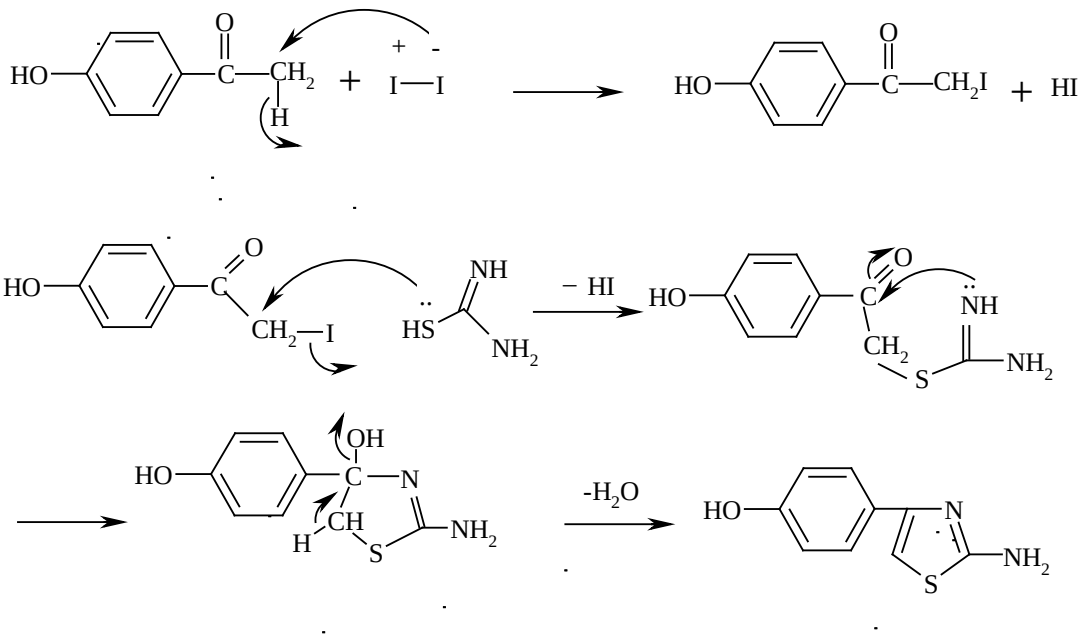
These compounds were synthesized using the same procedure given for compounds $[VI]_n$, except using the compound[XI] instead of compound [V] and used (0.002 mol) from different aromatic aldehyde, recrystallized from ethanol.
The physical data are given in Table 3.

Synthesis of Thiazolidin-4-one derivatives $[XIII]_n$

These compounds were synthesized by using the same procedure given for compounds $[VII]_n$, except using the compounds$[XII]_n$ instead of compounds $[VI]_n$ and used (0.02 mol) from thioglycolic acid, recrystallized from acetone .The physical data are given in Table 4.

Results and Discussion

The compound [I] was synthesized from fusion 4-hydroxy acetophenone with thiourea in iodine (I_2). The suggested mechanism of this reaction may be as follows, Scheme 3.



Scheme 3

The compound [I] was characterized by melting point ,FTIR and ^{1}HNMR. The characteristic FTIR absorption bands of compound [I] showed the disappearance absorption bands at 1662 cm^{-1} due to C=O stretching of 4-hydroxy acetophenone with the appearance of three a stretching bands at 3450 cm^{-1},3302 $cm^{-1}$and 3199 cm^{-1} due to υ NH, NH_2 bonds and appearance of a stretching band at 1622 cm^{-1} due to υ C=N for thiazole ring moiety. The ^{1}HNMR spectrum (in DMSO as a solvent) showed the following signals: a single at signal at δ 9.53 ppm for one proton could be attributed to the OH group, two doublet pairs in regain δ (6.75-7.82) ppm due to four aromatic protons, a broad signal at δ 7. 57 ppm for two protons of NH_2 group[16]. The signals δ6.78 ppm for one proton of thiazole ring[17] .

The compound[II] was synthesized by the reaction of compound [I] with pentoxy bromide in alkaline media.The FTIR spectrum of compound [II] showed disappearance of a band of υ OH group and appearance of new absorption stretching bands of the aliphatic υ C-H group in the region 2945-2860 cm^{-1} for alkyl groups.

Elemental analysis result of compound[II] is in good agreement with the theoretical data
Elemental analysis of compound[II] :
Calc. : C% = 65.11 , H% = 6.97 , N% = 10.85 , S% = 12.40
Found : C% =64.84 , H% = 6.64 , N% = 10.55 , S% = 12.61
The azo compound [III] was synthesized by coupling between diazonium salt of the amino thiazole [II] with phenol at 0-4˚C .

Diazonium coupling reactions are typical electrophilic aromatic substitutions in which the positively charged diazonium ion in the electrophile that reacts with the electron-rich ring of a phenol. Theis reaction usually occurs at the para position**.**The characteristic FTIR absorption bands of compound[III] showed the disappearance of two absorption bands due to NH_2 stretching of amine compound together with the appearance of a stretching broad band around 3381 cm^{-1} due to the intermolecular hydrogen bonding of υ O-H band. It also shows a band at 1537 cm^{-1} which is due to the υ N=N group.

The new compound[IV] was synthesized by the reaction of compounds[III] with ethyl α -chloroacetate in fused sodium acetate **.** The FTIR spectrum of compound [IV] showed a significant band at 1732 cm^{-1} which could be attributed to stretching vibration of the carbonyl of ester group. They also showed the disappearance of absorption band due to υ O-H of compound [III].

The compound [V] was synthesized by the reaction of ester compound [IV] with hydrazine hydrate in ethanol.The FTIR spectrum of compound [V] showed a shift in the carbonyl stretching band to ester group of compound [IV] to 1666 cm-1 for amide group of compound [V], also showed three bands in the range (3421-3043) cm-1 which is assigned to asymmetric and symmetric bands of NH and NH_2groups.

The Schiff bases of compounds$[VI]_n$ were synthesized by the refluxing of compound [V] with different aromatic aldehydes in ethanol.

The new Schiff bases compounds were characterized by melting points , C.H.N.S analysis , FTIR , ^{1}HNMR and Mass spectroscopy for compound$[VI]_1$.The characteristic FTIR absorption bands of series $[VI]_n$ showed the disappearance of two absorption bands due to NH_2 stretching of acid hydrazide together with the appearance of a stretching bands in the range at(1647-1655) cm^{-1} assignable to υ C=N. The Characteristics FTIR absorption bands of new Schiff bases$[VI]_n$ are listed in Table(5).

Elemental analysis of compound $[VI]_6$:

Calc. : C% = 66.98 , H% = 6.53 , N% = 11.16 , S% = 5.10
Found : C% = 67.12 , H% = 6.94 , N% = 11.32 , S% = 5.02

The above values are consistent with their proposed structure .

The^{1}HNMR spectrum(in $CDCl_3$ as a solvent) for compound$[VI]_3$ showed the following signals: : a sharp singlet signal at δ8.60 ppm that could be attributed to the azomethaine proton. Two doublets in the region δ (6.93-7.77) ppm due to twelve aromatic protons of phenyl rings and the one proton of thiazole ring overlap with aromatic protons of benzene rings , signal at δ (3.95-3.99)ppm is assigned for four protons of two OCH_2 groups and proton of NH group ,multiplate signal in region δ(1.77-1.89) ppm due to eight protons of CH_2 groups and two protons of $-CH_2C=O$ group appear at δ 2.16 ppm ,triplate signal at δ(1.02-1.07) ppm for six protons of two CH_3 groups.

The mass spectrum of compound $[VI]_1$(M.Wt=557) showed several peaks attributed to the presence of thiazole derivative as in Figure 1, showed two interesting peaks at m/z =269 (base peak) and m/z =393.Also showed most characteristic fragment at m/z =309 due to the cleavage of thaizole ring (HN=CH-Ar) , this is a good evidence for the presence of thaizole ring[18].

In addition showed another fragments at m/z=383 and m/z=369 ,this is another evidence for the presence of thaizole ring [19].

The thiazolidin-4-ones derivatives $[VII]_n$ were synthesized by refluxing equimolar amounts of the Schiff bases $[VI]_n$ with thioglycolic acid in dry benzene.

These compounds were characterized by their melting points, C.H.N.S. analysis ,FTIR and ^{1}HNMR spectroscopy.The FTIR spectra of compounds $[VII]_n$ showed the disappearance of a stretching band of imine group and appearance of stretching band due to a carbonyl group of thiazolidinone around (1710-1705) cm^{-1} and the FTIR spectra showed a band in (904-898) cm^{-1} for C-S stretching. This was the most characteristic evidence for the success of cyclization step. The FTIR spectral data for these compounds are listed in Table 6.

Elemental analysis of compound$[VII]_6$:

Calc. : C% = 63.33 , H% = 6.13 , N% = 9.98 , S% = 9.12
Found : C% = 63.36 , H% = 6.18 , N% = 10.20 , S% = 9.71

This result is consistent with its proposed structure.

^{1}HNMR spectrum of compound$[VII]_5$ (in DMSO as a solvent) showed the following characteristics chemical shifts : a signal at δ 8.12 ppm for proton of NH group ,multiplet signal in region δ (6.90-7.70) ppm for twelve aromatic protons of the benzene rings, signal at δ 6.55 ppm for proton of thiazole ring , a singlet was observed at δ5.70 ppm that could be assigned to the proton of H-2 thiazolidinone , another singlet signal appeared at δ 5.60 ppm due to proton of H-5 thiazolidinone. Also the ^{1}HNMR spectrum show signal observed

between δ (3.73-3.95) ppm was assigned to four protons of two methylene groups ($O-CH_2$) ,multiplet at δ(0.87-1.69) ppm could be attributed to eighteen protons of two $(CH_2)_3CH_3$ groups .Finally a sharp singlet signal appears at δ 4.40 ppm for two protons of $-CH_2C=O$ group .

The compound [VIII] was synthesized from fusion 4-aminoacetophenone with thiourea in iodine (I_2) .This compound was characterized by melting point and FTIR. The FTIR spectrum of compound [VIII] showed the disappearance absorption stretching bands of carbonyl group C=O and C=S of 4-aminoacetophenone and thiourea with the appearance of a stretching bands in reign(3304- 3182) cm^{-1} due to υ NH ,NH_2 groups and appearance a new stretching band at 1624 cm^{-1} due to υ C=N for thiazole ring moiety.

While, the compound [IX] was synthesized by the reaction of one mole of compound [VIII] with HNO_2 at 0-4˚C to get diazonium salt, which was reacted with two mole of phenol at the same temperature . The FTIR spectrum of this compound[IX] showed the disappearance of two absorption bands due to NH_2 stretching of amine compound [VIII] together with the appearance of a stretching two broad bands at 3404 $cm^{-1}$and 3340 cm^{-1} due to the intermolecular hydrogen bonding of υ O-H bond. It also shows a band at 1516 cm^{-1} which is due to the υ N=N group.

The reaction of compound[IX] with two moles from ethyl α-chloroacetate in basic medium yielded a new compound[X]. This compound identified by melting point and FTIR spectroscopy. The FTIR spectrum of compound [X] showed a significant band at 1730 cm^{-1} which could be attributed to stretching vibration of the carbonyl of ester groups, they also showed the disappearance absorption band due to υ O-H group for compound [XI].

The acid hydrazide [XI] is produced from the condensation of ester compound [X] with two moles hydrazine hydrate in ethanol. This compound is identified by melting point and FTIR spectroscopy.The FTIR spectrum of this compound showed the disappearance of absorption band of carbonyl for ester group and the appearance of a new band at 1666 cm^{-1} due to stretching vibration carbonyl for amide group, also showed three bands in the region (3387-3188) cm^{-1} due to asymmetric and symmetric of NH and NH_2 groups.

The new Schiff bases $[XII]_n$ were synthesized by refluxing one mole of compound [XI] with two moles of n-4-alkoxy benzaldehyde in absolute ethanol. The new Schiff bases compounds were characterized by melting points , FTIR spectroscopy. The characteristic FTIR absorption bands showed the disappearance of two absorption bands due to NH_2 group together with the appearance of a stretching bands in region (1656- 1650) cm^{-1} assignable to υ C=N group.The Characteristics FTIR absorption bands of these compounds$[XII]_n$ are given in Table(7).The compounds$[XIII]_n$ were synthesized by the reaction of two moles of thioglycolic acid with one mole of Schiff bases $[XII]_n$ in dry benzene. The compounds were characterized by their melting points and FTIR spectroscopy. The FTIR spectra showed the disappearance of a stretching band of imine groups and the appearance of a stretching band of carbonyl group of thiazolidinone moiety around (1712-1716) cm^{-1} and C-S groups around (902- 906) cm^{-1}. The FTIR spectral data for these compounds are listed in Table (8).

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Table(1):the physical properties for the compounds$[VI]_n$

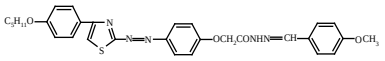
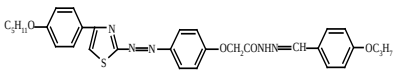
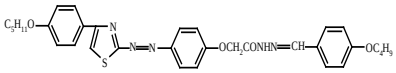
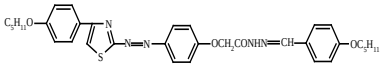
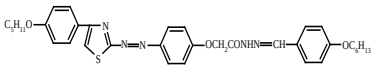
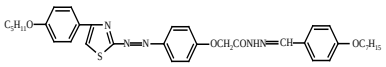
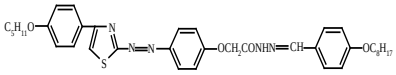
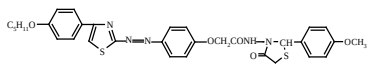
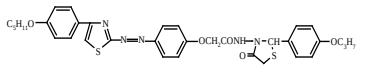
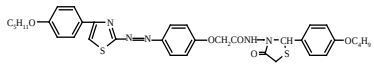
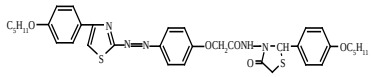
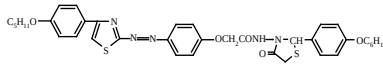
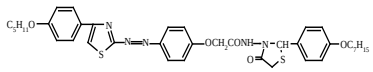
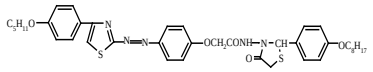
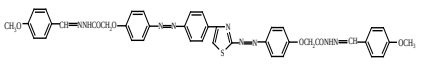
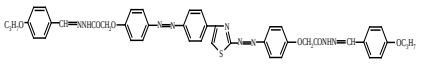
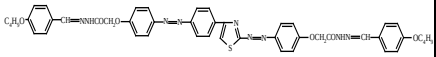
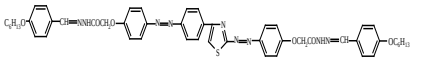
Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P ^0C	Yield %	Color
$[VI]_1$	2-[4`-(4``-methoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{30}H_{31}O_4N_5S$	159-160	88	Pal yellow
$[VI]_3$	2-[4`-(4``-propoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{32}H_{35}O_4N_5S$	143-145	79	Pal yellow
$[VI]_4$	2-[4`-(4``-butoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{33}H_{37}O_4N_5S$	132-134	85	Yellow
$[VI]_5$	2-[4`-(4``-pentoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{34}H_{39}O_4N_5S$	120-121	75	Pal yellow
$[VI]_6$	2-[4`-(4``-hexoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{35}H_{41}O_4N_5S$	117-118	80	Pal yellow
$[VI]_7$	2-[4`-(4``-heptoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{36}H_{43}O_4N_5S$	> 295	70	Pal yellow
$[VI]_8$	2-[4`-(4``-octoxy benzaledine amino)-oxyacetamide] phenyl azo-4-(4```-n-pentoxyphenyl)-1,3-thiazole		$C_{37}H_{45}O_4N_5S$	99-101	83	Pal yellow

Table (2):The physical properties for the compounds$[VII]_n$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P ^0C	Yield %	Color
$[VII]_1$	2-{4`-[2-(4``-methoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl} azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{32}H_{33}O_5N_5S_2$	230-232	64	Off white
$[VII]_3$	2-{4`-[2-(4``-propoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl} azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{34}H_{37}O_5N_5S_2$	gummy	70	Off white
$[VII]_4$	2-{4`-[2-(4``-butoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl} azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{35}H_{39}O_5N_5S_2$	gummy	74	Off white
$[VII]_5$	2-{4`-[2-(4``-pentoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl} azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{36}H_{41}O_5N_5S_2$	gummy	70	pink
$[VII]_6$	2-{4`-[2-(4``-hexoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl }azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{37}H_{43}O_5N_5S_2$	gummy	65	Off white
$[VII]_7$	2-{4`-[2-(4``-heptoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl }azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{38}H_{45}O_5N_5S_2$	gummy	63	Pal brown
$[VII]_8$	2-{4`-[2-(4``-octoxyphenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl }azo-4-(4```-pentoxyphenyl)-1,3-thiazole		$C_{39}H_{47}O_5N_5S_2$	> 290	68	pink

Table(3):The physical properties of compounds[XII]$_n$

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P ^{0}C	Yield %	Color
[XII]$_1$	2-[4`-(4``-methoxy benzaledine amino)-oxy acetamide] phenyl azo-4-[4```-(4````-methoxy benzaledineamino)-oxy acetamide phenyl azo] phenyl -1,3-thiazole		$C_{41}H_{35}O_6N_9S$	160-162	83	yellow
[XII]$_3$	2-[4`-(4``- propoxy benzaledine amino)-oxy acetamide] phenyl azo-4-[4```-(4````-propoxy benzaledineamino)-oxy acetamide phenyl azo] phenyl -1,3-thiazole		$C_{45}H_{43}O_6N_9S$	140-141	79	pal brown
[XII]$_4$	2-[4`-(4``- butoxy benzaledine amino)-oxy acetamide] phenyl azo-4-[4```-(4````-butoxy benzaledineamino)-oxy acetamide phenyl azo] phenyl -1,3-thiazole		$C_{47}H_{47}O_6N_9S$	120-122	80	pal brown
[XII]$_6$	2-[4`-(4``- hexoxy benzaledine amino)-oxy acetamide] phenyl azo-4-[4```-(4````-hexoxy benzaledineamino)-oxy acetamide phenyl azo] phenyl -1,3-thiazole		$C_{51}H_{55}O_6N_9S$	90-92	75	yellow

Table(4):The physical properties of compounds[XIII]$_n$

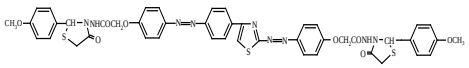
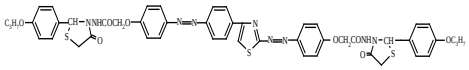
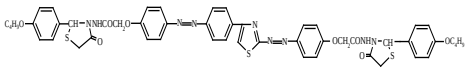
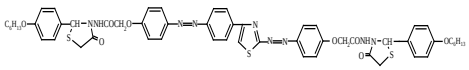
Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P ^{0}C	Yield %	Color
[XIII]$_1$	2-{4`-[2-(4``-methoxy phenyl)-3-oxyacetamide)thiozoliden-4-one]phenyl }azo-4-{4```-[2-(4````- methoxy phenyl)-3-(oxyacetamide) thiozoliden-4-one]phenyl azo }phenyl-1,3-thiazole		$C_{45}H_{39}O_8N_9S_2$	gummy	70	pal yellow
[XIII]$_3$	2-{4`-[2-(4``-propoxy phenyl)-3-oxyacetamide)thiozoliden-4-one]phenyl }azo-4-{4```-[2-(4````- propoxy phenyl)-3-(oxyacetamide) thiozoliden-4-one]phenyl azo }phenyl-1,3-thiazole		$C_{49}H_{47}O_8N_9S_2$	gummy	67	pal yellow
[XIII]$_4$	2-{4`-[2-(4``-butoxy phenyl)-3-oxyacetamide)thiozoliden-4-one]phenyl }azo-4-{4```-[2-(4````- butoxy phenyl)-3-(oxyacetamide) thiozoliden-4-one]phenyl azo }phenyl-1,3-thiazole		$C_{51}H_{51}O_8N_9S_2$	gummy	64	pal yellow
[XIII]$_6$	2-{4`-[2-(4``-hexoxy phenyl)-3-oxyacetamide)thiozoliden-4-one]phenyl}azo-4-{4```-[2-(4````-hexoxy phenyl)-3-(oxyacetamide)thiozoliden-4-one]phenyl azo}phenyl-1,3-thiazole		$C_{55}H_{59}O_8N_9S_2$	gummy	72	pal yellow

Table (5) : Characteristics FTIR absorption bands of compounds[VI]$_n$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})						
	ʋNH	ʋ(C-H) aromatic	ʋ(C-H) aliphatic	ʋ(C=O) amide	ʋ(C=N) exocyclic	ʋ(C=N) endocyclic	ʋ (C=C) aromatic
[VI]$_1$	3309	3030	2904-2839	1683	1647	1625	1602
[VI]$_3$	3377	3040	2964-2877	1668	1650	1624	1600
[VI]$_4$	3300	3039	2960-2841	1683	1654	1624	1602
[VI]$_5$	3365	3035	2953-2868	1650	1645	1624	1602
[VI]$_6$	3375	3049	2993-2858	1685	1660	1620	1606
[VI]$_7$	3300	3035	2940-2860	1675	1660	1622	1604
[VI]$_8$	3315	3072	2924-2854	1670	1655	1622	1604

Table (6) : Characteristics FTIR absorption bands of thiazoldin-4-ones[VII]n

Comp No.	Characteristic bands FTIR spectra(cm^{-1})						
	U (N-H)	U(C-H) benzylic	U(C- H) aliphatic	U(C=O) thiazoldinone	U(C=O) amide	U(C=C) aromatic	U(C-S)
$[VII]_1$	3332	3251	2958-2854	1705	1674	1604	898
$[VII]_3$	3325	3178	2962-2854	1718	1676	1608	902
$[VII]_4$	3242	3190	2956-2854	1714	1678	1605	904
$[VII]_5$	3280	3190	2954-2870	1720	1668	1608	906
$[VII]_6$	3240	3190	2954-2858	1712	1670	1608	902
$[VII]_7$	3350	3155	2956-2854	1716	1670	1603	898
$[VII]_8$	3329	3182	2954-2854	1710	1676	1602	904

Table(7):Characteristics FTIR absorption bands of compounds $[XII]_n$

Comp. No.	Characteristic bands FTIR spectra(cm^{-1})						
	UNH	U(C-H) aromatic	U(C-H) aliphatic	U(C=O) Amide	U(C=N) exocyclic	U(C=N) endocyclic	U(C=C) aromatic
$[XII]_1$	3310	3012	2985-2839	1665	1656	1625	1602
$[XII]_3$	3331	3010	2964-2877	1664	1641	1624	1602
$[XII]_4$	3317	3037	2980-2875	1656	1645	1624	1602
$[XII]_6$	3313	3049	2945-2860	1678	1650	1622	1606

Table(8) : Characteristics FTIR absorption bands of thiazoldin-4-one [XIII]n

Comp No.	Characteristic bands FTIR spectra(cm^{-1})						
	U(N-H)	U(C-H) aromatic	U(C- H) aliphatic	U(C=O) thiazoldinone	U(C=O) amide	U(C=C) aromatic	U(C-S)
$[XIII]_1$	3346	3007	2970-2837	1712	1670	1583	902
$[XIII]_3$	3410	3028	2968-2875	1712	1680	1608	904
$[XIII]_4$	3310	3040	2958-2875	1716	1650	1610	898
$[XIII]_6$	3390	3030	2931-2821	1716	1670	1602	906

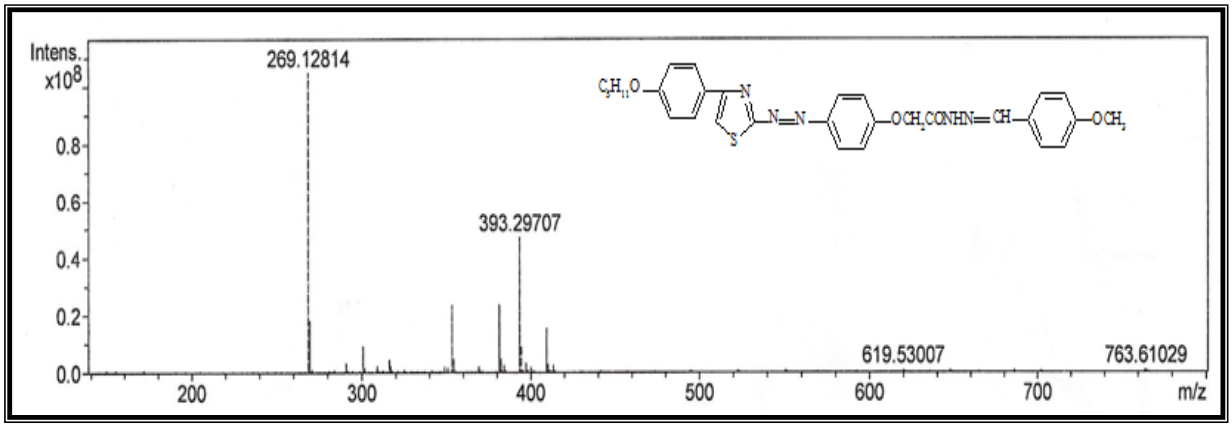


Figure No.(1): Mass spectrum of compound $[VI]_1$

تحضير مركبات حلقية غير متجانسة مشتقة من4- هيدروكسي و4 – أمينو أسيتوفينون وتشخيصها

نسرين حسين كرم
جمبد هرمز توما
عمار هاني الدجيلي
قسم الكيمياء /كلية التربية– للعلوم الصرفة (ابن الهيثم) / جامعة بغداد

استلم البحث في : 23 حزيران 2013 ، قبل البحث في : 26 آب 2013

الخلاصة

تم في هذا البحث تحضير سلسلتين قواعد شف$_n$[VI] ومشتقات الثايوزولدين-4- ون$_n$[VII] وذالك بعدد من الخطوات تبدأ بتفاعل 4– هيدروكسي أسيتوفينون مع الثايويورايا واليود لينتج المركب 3,1-ثايوزول[I] الذي يتفاعل مع بنتوكسي برومايد وكاربونات البوتاسيوم اللامائية في الاسيتون لينتج المركب [II]وهذا يتفاعل مع الفينول لينتج مركب الازو[III].والذي بدوره يتفاعل مع اثيل كلورواسيتيت في وسط قاعدي لينتج مركب استري جديد[IV] والذي تمت مفاعلته مع الهيدرازين لينتج حامض الهيدرازايد[V]. والمركب الاخير يتكاثف مع نورمل الكوكسي بنزالديهايد ليعطي قواعد شف جديدة$_n$[VI] .ومجموعة الايمين تدخل اضافة حلقة مع حامض الثايوكلايكولك لتعطي مركبات الثايوزولدين-4-ون$_n$[VII] وكذالك حضيرت سلسلتين جديدة من قواعد شف$_n$[XII] ومشتقات الثايوزولدين-4- ون$_n$[XIII] وذلك بعدد من الخطوات المشابهة لتحضير قواعد شف $_n$[VI] والثايوزولدين-4- ون$_n$[VII] عدا استعمال 4– أمينو أسيتوفينون بدل 4– هيدروكسي أسيتوفينون . شخصت جميع المركبات المحضرة بوساطة درجات انصهارها، ، تحليل العناصر ، طيف FTIR ، طيف ^{1}HNMR وطيف الكتلة لبعض منها.

الكلمات المفتاحية: الثايوزول ،الثايوزولدينون، مركبات حلقية غير متجانسة ، قواعد شف