

Synthesis and Characterization of Novel Schiff Bases Containing Isoxazoline or Pyrazoline Unit

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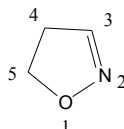
Abstract

This work involves synthesis of novel Schiff bases derivatives containing isoxazoline or pyrazoline units starting with chalcones . 4-Aminoacetophenone was react with p-nitrobenzaldehyde or p-chlorobenzaldehyde in basic medium giving chalcones [I]_{a,b} by claisen-schmidt reactions. The chalcones [I]_{a,b} were reacted with hydroxylamine hydrochloride giving isoxazolines [II]_{a,b} in basic medium. The chalcone [I]_a could also reacted with hydrazine hydrate to give pyrazolines [III]_a . The novel Schiff bases with structural formula [VIII]_n , [IX]_n , [X]_m and [XI]_m were prepared by the reaction of amino compounds ; isoxazoline [II]_{a,b} and pyrazolines [III]_a with monoaldehydes [VI]_n and dialdehydes [VII]_m , respectively in dry benzene using drops of glacial acetic acid as a catalyst with reflux . All the synthesized compounds have been characterized by melting points , FTIR , UV-Vis and ¹HMR (of some of theme) spectroscopy.

Key word : isoxazoline , pyrazoline , Schiff bases.

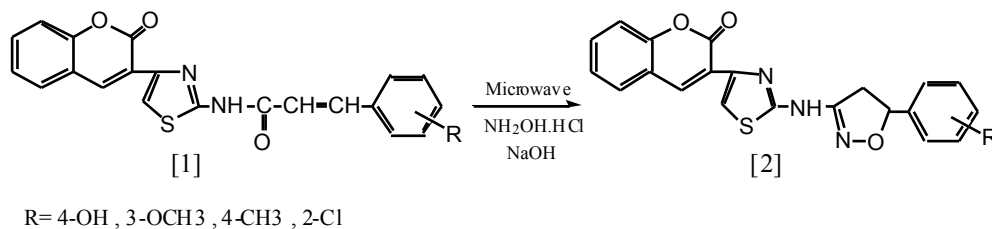
Introduction

Isoxazolines are heterocyclic organic compounds that contain oxygen and nitrogen atoms at position 1 and 2 .

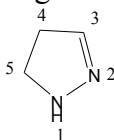


The classical synthesis of the isoxazolines involves the base-catalyzed condensation of substituted aromatic ketone and substituted aldehydes to give α,β -unsaturated ketones (chalcone), which on cyclization with hydroxylamine hydrochloride in alkaline medium give the corresponding isoxazoline derivatives. (1-3).

Desai et .al (4) synthesized of isoxazoline derivatives [2] from substituted chalcones [1] using hydroxylamine hydrochloride in NaOH medium using microwave .



pyrazolines are heterocyclic compound of five membered unsaturated ring structure composed of three carbon atoms and two nitrogen atoms at position 1 and 2 .



Synthesis and characterization of pyrazoline(5,6) derivatives has been a developing field within the realm of heterocyclic chemistry, because of their diverse properties, fairly assessable path of synthesis, wide range of therapeutic activities and variety of industrial application, the pyrazoline and ring became a center of attraction for organic chemists.

Various methods were used for the preparation of pyrazolines , treatment of α,β -unsaturated ketones with hydrazines seems to be the most popular procedure for this purpose , this reaction has been conducted under various conditions (7-12). Pyrazoline derivatives are important electron rich nitrogen heterocycles which play an important role in the diverse biological activities. These nitrogen heterocycles widely occur in nature in the form of alkaloids, vitamins, pigments and as constituents of plant and animal cells.

Isoxazoline and pyrazoline derivatives remain a main focus of medicinal chemist, due to their diverse pharmacological activity. Isoxazoline and pyrazolines derivatives have been reported to possess antibacterial(11), antifungal(4,13), and antimicrobial(14,15) activity. In addition, isoxazoline derivatives have played a crucial role as intermediates in the organic synthesis of number of heterocyclic pharmacological active compounds(16).

Schiff bases attract much interest both for synthetic and biological point of view (17). Through literature survey reveals that Schiff bases derived from various heterocyclic possess cytotoxic (18) , anticonvulsant , antimicrobial (19, 20) , antiproliferative (17) , anticancer (21) , and antifungal (22) activities .

Depending on the above finding , we decided to synthesize novel Schiff bases containing isoxazoline or pyrazoline units.

Experimental

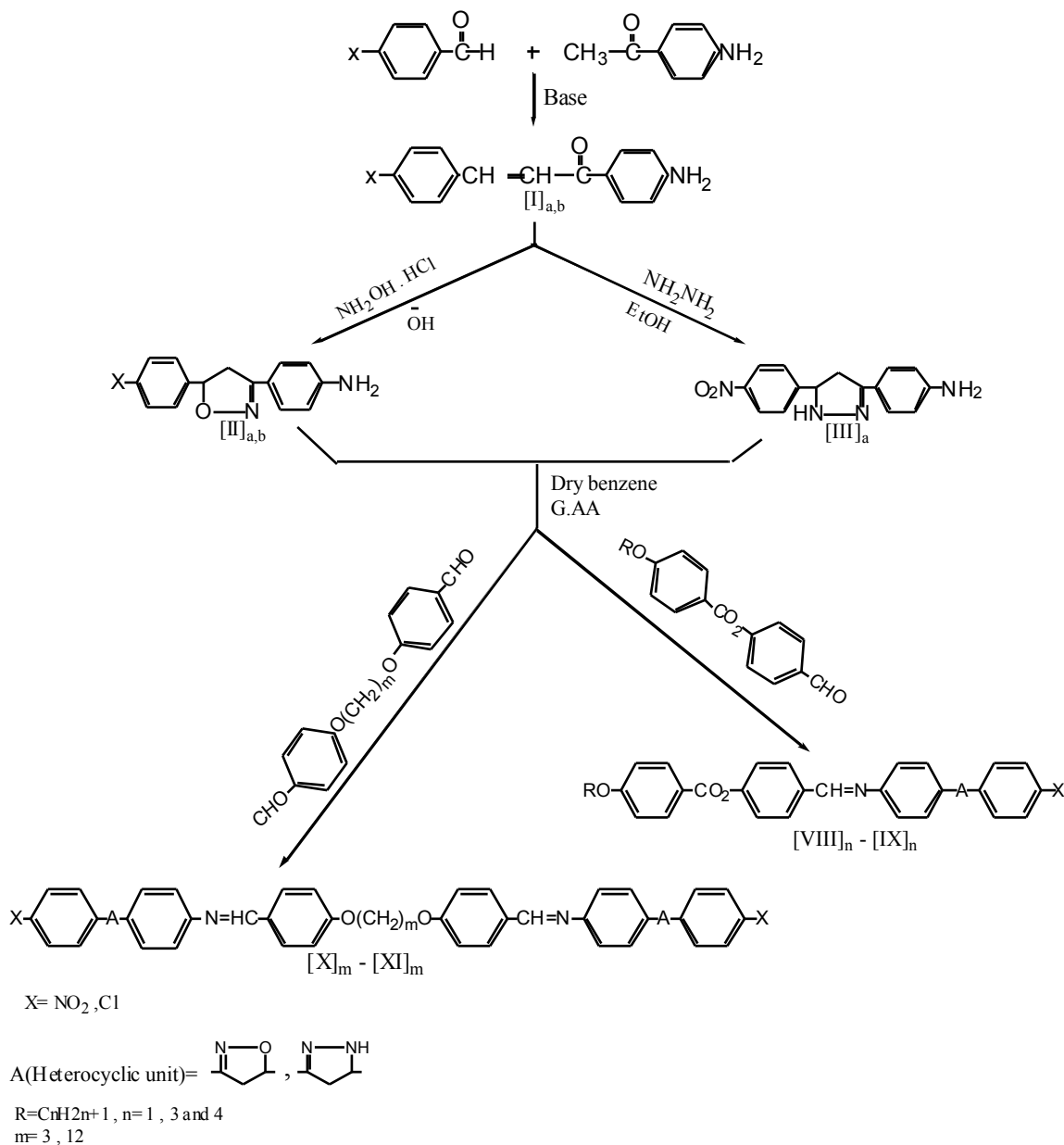
Materials : All the chemicals were supplied from Merck , GCC and Aldrich Chemicals Co. and used as received .

Techniques : FTIR spectra were recorded using potassium bromide discs on a 8400s Shimadzu spectrophotometer and FTIR spectrophotometer , Shimadzo (Ir prestige-21) . ¹HNMR spectra were carried out by company : Bruker , model: ultra shield 300 MHz , origin : Switzerland and are reported in ppm(S), DMSO was used as a solvent with TMS as an internal standard . Measurements were made at chemistry department, Al-albyat university , Uncorrected

melting points were determined by using Hot-Stage, Gallen Kamp melting point apparatus. UV spectra of solutions were performed on CECL 7200 England Spectrophotometer using CHCl_3 as a solvent .

General procedures

Compounds $[\text{VIII}]_n$, $[\text{IX}]_n$, $[\text{X}]_m$ and $[\text{XI}]_m$ were synthesized according to Scheme 1.



Scheme 1

Preparation of (chalcone) 4-[3-(4'-substituted phenyl)-2-propene-1-one]-aniline $[\text{I}]_{a,b}$

Equimolar quantities of 4-amino acetophenone (1.35gm , 0.01 mol) and 4-chloro benzaldehyde or 4- nitro benzaldehyde (0.01 mol) were dissolved in minimum amount of alcohol. Sodium

hydroxide solution (0.02 mol) was added slowly and the mixture becomes cold. Then the mixture was poured slowly into 400mL of ice water with constant stirring and kept in refrigerator for 24 hrs (23). The precipitate obtained was filtered, washed and recrystallized from chloroform. The physical properties are given in table 1.

Preparation of 4[5-(4'-substituted phenyl)-4,5-dihydroisoxazol-3-yl] aniline [II]_{a,b}

A mixture of chalk one [I]_a or [I]_b (0.02 mol), hydroxylamine hydrochloride (1.39 gm, 0.02 mol) and sodium hydroxide solution (0.5 gm NaOH in 25 mL of water) in ethanol (60mL) was refluxed for 6hrs. The mixture was concentrated under vacuum and poured into ice water. The precipitate obtained was filtered, washed and recrystallized from ethanol (24) physical data are listed in Table (2.1).

Preparation of 4[5-(4'-nitro phenyl)-4,5-dihydro-1H-pyrazol-3-yl]-aniline [III]_a A mixture of chalcone [I]_a, (0.01 mol) and hydrazine hydrate (0.5g, 0.01 mol) in ethanol (15 mL) was heated under reflux for 6hrs. After cooling the separated solid was filtered off, dried and crystallized from ethanol (24) physical properties listed in Table (2.1).

preparation of n-alkoxy benzoic acid [IV]_n : This compound was prepared according to references (25).

n-alkoxybenzoyl Chloride [V]_n : General procedure for preparation of carboxylic acid chlorides was described by A. Vogel (26).

Preparation of 4(4'-n-alkoxy benzoyloxy) benzaldehyde [VI]_n

Acid chloride [V]_n (10 mmol) was added to a stirred solution of 4-hydroxy benzaldehyde (10 mmol) and dry pyridine (1mL) in dry dimethyl formamide (DMF) (10 mL) at (5-10°C). Stirring was continued for 3hrs at the same temperature. The resulting mixture was poured into 100 mL of 10% HCl. The precipitate was filtered and washed with solution of 10% NaHCO₃ and water for several times (27), dried and recrystallized from ethanol.

Preparation of polymethylene- α,ω -bis-4-oxo benzaldehydes [VII]_m

These compounds were prepared following the procedure described by A. Griffin et al. (28).

Synthesis of Schiff bases.

Mono Schiff bases [VIII]_n – [IX]_n

A mixture of new amino compounds [II]_{a,b} or [III]_{a,b} (0.01 mol), aldehyde [VI]_n (0.012 mol), dry benzene (15 mL) and 2 drops of glacial acetic acid was refluxed for 3hrs. The solvent was evaporated under vacuum and the residue crystallized from chloroform. The physical data of these Schiff bases are listed in Table (1).

Bis Schiff bases [X]_m – [XI]_m

These compounds [X]_m – [XI]_m were obtained by using the same procedure given for the synthesis of 4 Schiff bases [VIII]_n – [IX]_n except the dialdehyde [VII]_m was used instead of monoaldehyde [VI]_n. The physical properties of all these bis 4 Schiff bases are given in Table (1).

Results and Discussion

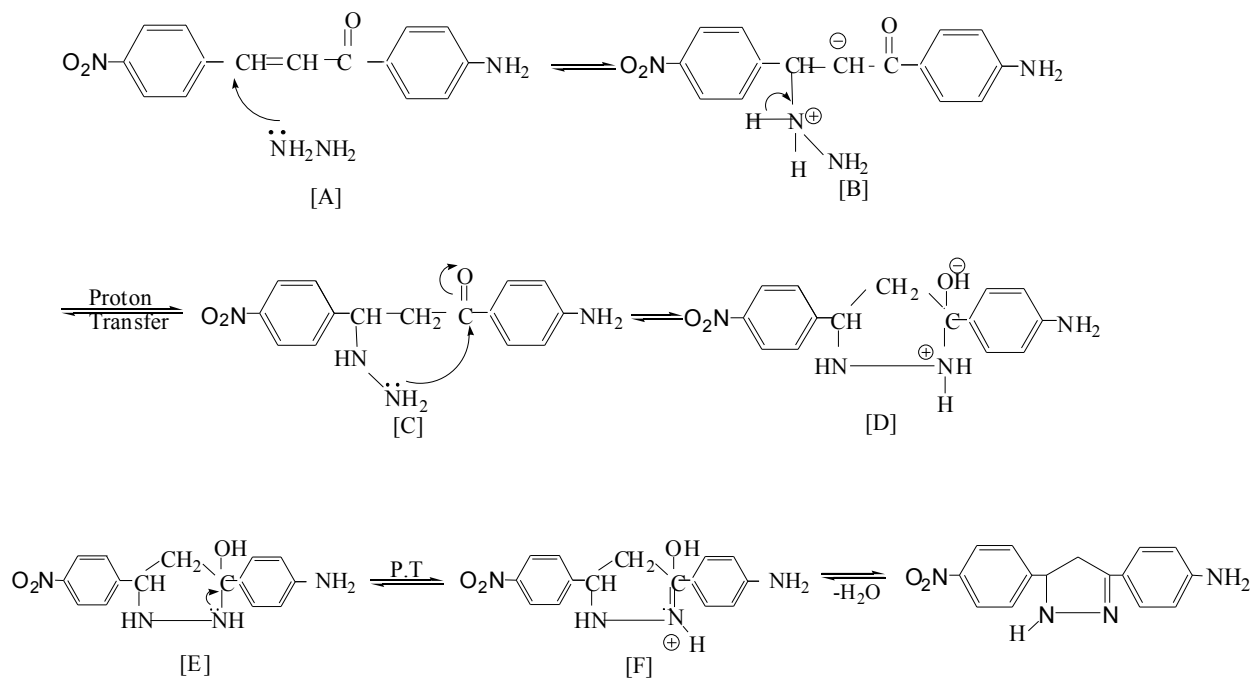
Chalcone was chosen as the starting material for the synthesis of different heterocyclic compounds, such as: isoxazolines, pyrazolines derivatives by using appropriate reagents for that purpose.

The chalcones [I]_{a,b} are synthesized by Claisen-Schmidt condensation of 4-aminoacetophenone and p-substituted benzaldehyde by base catalyzed followed by dehydration to yield the desired chalcones. The structural assignments of the chalcones [I]_{a,b} based on melting points and their spectral data of FTIR, UV and ¹HNMR spectroscopy.

The FTIR spectra indicated the appearance of two bands in the region (3273-3483) cm⁻¹ which could be attributed to asymmetric and symmetric stretching vibration of NH₂ group, a weak band at 3105-3119 cm⁻¹ due to stretching vibration of (=C-H) group, two peaks at 1650 cm⁻¹ and 1635 cm⁻¹ due to C=O and C=C (CH=CH) stretching vibrations, respectively. The UV-VIS spectroscopy of two chalcones [I]_a and [I]_b exhibited λ_{max} at 306 nm and 341.5 nm, respectively.

The ¹HNMR of chalcone [I]_a shows the following features: two pairs of doublets in the region δ 7.6-8.2 ppm which can be attributed to eight protons of two p-substituted benzene rings having different substituents at positions 1,4. A doublet band at δ 6.6 ppm due to two protons of COCH= moiety and a doublet band at δ 8.3 ppm for protons of =CHAr (1). The two protons of the amine group appear as a singlet band at δ 6.24 ppm.

This compound [II]_{a,b} was synthesized from the reaction of chalcones [I]_{a,b} with hydroxylamine hydrochloride in alkaline medium. Scheme 2, the mechanism of this reaction (29) may be outlined as follows Scheme 2.



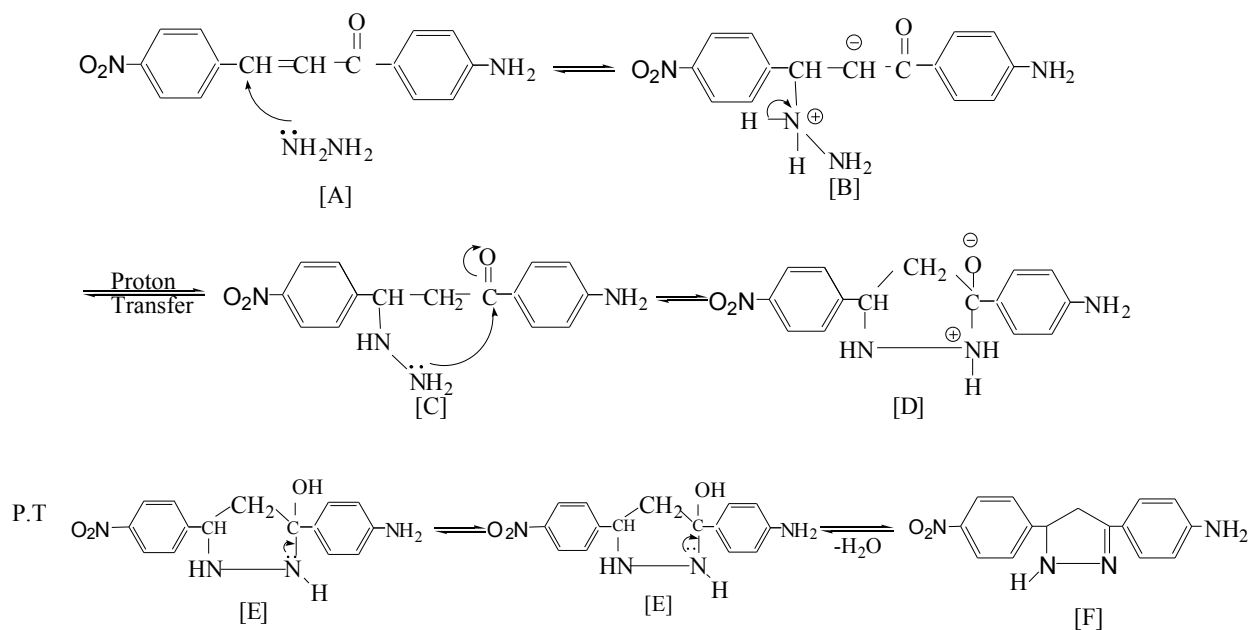
Scheme 3

The reaction proceeds via nucleophilic attack of the hydroxyl (OH) group of hydroxyl amine upon the carbon-carbon double bond in the basic medium (NaOH) to give the carbonion intermediate [A]. Proton transfer yielded [B], followed by intramolecular addition of the amino group on carbonyl carbon of [B] whole yield the intermediate [D]. Loss of H₂O gives the isoxazoline compounds [E].

The structure of the isoxazolines [II]_{a,b} have been characterized by melting point , FTIR,UV and ¹HNMR spectroscopy. The FTIR spectra of isoxazolines [II]_{a,b} showed the disappearance of two absorption bands of the CH=CH and C=O group in the starting material [I]_{a,b} together with appearance of new absorption bands for C=N and C-O (cyclic ether) groups around 1628 cm⁻¹ and 1180 cm⁻¹, respectively. The UV-VIS spectroscopy of isoxazolines [II]_a and [II]_b exhibited λ_{max} at 301.5 nm and 293.5 nm ,respectively.

The ¹HNMR spectrum of compound [II]_b shows the following singals : eight aromatic proton appeared as multiplate at δ7.2-7.9 ppm , a singlet at δ 5.76 ppm due to the two protons of amino group. One proton of CH-(isoxazoline) appeared as doublet at δ 6.0-6.3 ppm. While the two protons of CH₂ (isoxazoline) appears as doublet of doublet at δ 2.5 ppm (29).

The chalcone [I]_a was further reacted with hydrazine hydrate in ethanol absolute to yield the corresponding pyrazoline derivatives by the following reaction mechanism (30) , scheme 3.



Scheme 3

Condensation of chalcone with hydrazine hydrate in abs.ethanol under reflux afforded the addition product [C] which followed by closure reaction led to formation new pyrazoline [F] .

The structure of the pyrazoline [III]_a was identified by melting point , FTIR,UV and ¹HNMR spectroscopy. The FTIR spectrum of this compound showed the disappearance of two absorption bands of the CH=CH and C=O group ,in the chalcone [I]_a ,and appearance of new absorption bands of NH and C=N group at 3379 cm⁻¹ and 1620 cm⁻¹, respectively. The UV-VIS spectroscopy of pyrazoline [III]_a exhibited λ_{max} at 302.5 nm .

The ^1H NMR spectrum of compound [III]_a shows the following signals : eight aromatic protons appeared as doublets at δ 7.3-8.2 ppm, a doublet at δ 6.5-6.6 ppm that could be attributed to the one proton of NH (pyrazoline). Sharp singlet at δ 5.3 ppm due to the two protons of amino group. One proton H_x of CH-(pyrazoline) appeared as triplet (24) at δ 4.8-4.95 ppm, while the protons of CH-(pyrazoline) appears as one pair doublet of doublets at δ 3.4-3.5 ppm and δ 2.5-2.8 ppm due to two protons of H_a and H_b, respectively .

The new Schiff bases [VIII]_n-[XI]_m were synthesized by refluxing aromatic primary amine [II]_{a,b} or [III]_a and mono-aldehyde [VI]_n or di-aldehyde [VII]_m in dry benzene with some drops of glacial acetic acid (GAA).

These Schiff bases were identified by their melting points , FTIR , UV and ^1H NMR spectroscopy . FTIR absorption-spectra showed the disappearance of absorption bands due to NH₂ and C=O groups of the starting materials together with appearance of new absorption band in the region (1625-1650) cm^{-1} which is assigned to C=N stretching.

The other data of functional groups which are characteristic of these compounds and the UV-VIS spectroscopy data are given in Table 2.

^1H NMR spectrum of Schiff base [X]_{12b} the shows the following signals: twenty four aromatic protons appeared as doublets in the region δ 6.6-7.9 ppm , sharp singlet at δ 6.2 ppm that could be attributed to azomethine protons . A singlet signal at δ 6.1 ppm is due to one proton of (CH) isoxazoline rings , three protons triplet at δ 4.95-5.2 ppm that are attributed to OCH₂ groups . Two protons of CH₂ (isoxazoline) appears as doublet of doublet at δ 4.1-4.5 ppm , and a multiplet at the region δ 1.0-2.1 which were assigned to the ten aliphatic protons of (CH₂)₁₀ .

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Table (1): The physical properties of Chalcones [I] and compounds [II]-[IV].

Comp. No.	Nomenclature	Structural formula	Molecular formula	M. P °C	Yield %	Color
[III] _a	4[5-(4'-nitrophenyl)-4,5-dihydroisoxazol-3-yl]aniline		C ₁₅ H ₁₃ N ₃ O ₃	230	50	Dark brown
[III] _b	4[5-(4'-chlorophenyl)-4,5-dihydroisoxazol-3-yl]aniline		C ₁₅ H ₁₃ N ₂ OCl	152	55	Pale yellow
[III] _a	4[5-(4'-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl]aniline		C ₁₅ H ₁₄ N ₄ O ₂	150	65	Orange
[VIII] _{1a}	3[4-(p-methoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydroisoxazole		C ₃₀ H ₂₃ N ₃ O ₆	242	50	Dark orange
[VIII] _{3a}	3[4-(p-propoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydroisoxazole		C ₃₂ H ₂₇ N ₃ O ₆	276	68	Dark orange
[VIII] _{4a}	3[4-(p-butoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydroisoxazole		C ₃₃ H ₂₉ N ₃ O ₆	240	80	Dark orange
[VIII] _{1b}	3[4-(p-methoxyBenzoyloxy) benzylidene aminophenyl]-5-(p-chlorophenyl)-4,5dihydroisoxazole		C ₃₀ H ₂₃ N ₂ O ₄ Cl	256-260	48	Pale yellow

[VIII] _{3b}	3[4-(p-propoxy benzoyloxy)benzylidene aminophenyl]-5-(p-chlorophenyl)-4,5-dihydroisoxazole		C ₃₂ H ₂₇ N ₂ O ₄ Cl	260	80	Pale yellow
[VIII] _{4b}	3[4-(p-butoxy benzoyloxy)benzylidene aminophenyl]-5-(p-chlorophenyl)-4,5-dihydroisoxazole		C ₃₃ H ₂₉ N ₂ O ₄ Cl	218-222	50	Pale brown
[IX] _{1a}	3[4-(p-methoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydro-1H-pyrazole		C ₃₀ H ₂₄ N ₄ O ₅	224	70	Dark brown
[IX] _{3a}	3[4-(p-propoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydro-1H-pyrazole		C ₃₂ H ₂₈ N ₄ O ₅	248	50	Dark brown
[IX] _{4a}	3[4-(p-butoxy benzoyloxy) benzylidene aminophenyl]-5-(p-nitrophenyl)-4,5-dihydro-1H-pyrazole		C ₃₃ H ₃₀ N ₄ O ₅	244-246	48	Dark brown
[X] _{3a}	1,3-bis{4-[5-(p-nitrophenyl)-4,5-dihydroisoxazol-3-yl] aniline-benzylidene -4oxy} propane		C ₄₇ H ₃₈ N ₆ O ₈	200	55	Brown
[X] _{12a}	1,12-bis{4-[5-(p-nitrophenyl)-4,5-dihydroisoxazol-3-yl] aniline benzylidene-4-oxy} dodecane		C ₅₆ H ₅₆ N ₆ O ₈	186	70	Dark orange

[X] _{3b}	1,3-bis{4-[5-(p-chlorophenyl)-4,5-dihydroisoxazol-3-yl] aniline-benzylidene-4oxy}propane		$C_{47}H_{38}N_4O_4Cl_2$	>300	51	Yellow
[X] _{12b}	1,12-bis{4-[5-(p-chlorophenyl)-4,5-dihydroisoxazol-3-yl] aniline bezylidene-4oxy}dodecane		$C_{56}H_{56}N_4O_4Cl_2$	256	84	Pale yellow
[XI] _{3a}	1,3-bis{4-[5-(p-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl] aniline benzylidene-4oxy}propane		$C_{47}H_{40}N_8O_6$	202	53	Dark brown
[XI] _{12a}	1,12-bis{4-[5-(p-nitrophenyl)-4,5-dihydro-1H-pyrazol-3-yl] aniline benzylidene-4oxy}propane		$C_{56}H_{58}N_8O_6$	210	50	Dark brown

Table (2): Characteristic FTIR absorption bands and UV data (λ_{\max}) of mono Schiff bases [XI]-[XIV].

Comp. No.	UV data	Characteristic bands FTIR spectra (cm-1)							
		λ_{\max} (nm) in CHCl ₃	ν NH	ν C-H aromatic	ν C-H aliphatic	ν C=O ester	ν C=N exocyclic	ν C=N endocyclic	ν C=C aromatic
[VIII] _{1a}	282		3071	2843-2950	1724	1630	1605	1585	1261
[VIII] _{3a}	278.5		3077	2841-2969	1728	1627	1601	1599	1258
[VIII] _{4a}	276.5		3071	2825-2959	1728	1630	1601	1582	1261
[VIII] _{1b}	281.5		3050	2820-2960	1728	1627	1601	1580	1261
[VIII] _{3b}	278		3070	2845-2960	1724	1627	1600	1597	1259
[VIII] _{4b}	277.5		3071	2874-2961	1726	1630	1607	1580	1261
[IX] _{1a}	277.5	3430	3050	2871-2959	1724	1627	1605	1582	
[IX] _{3a}	275.5	3418	3066	2878-2970	1724	1637	1600	1585	
[IX] _{4a}	278.5	3431	3071	2872-2961	1726	1627	1607	1590	
[X] _{3a}	290		3050	2850-2934		1627	1600	1589	
[X] _{12a}	287		3070	2851-2924		1628	1601	1597	
[X] _{3b}	334		3055	2853-2930		1630	1605	1598	
[X] _{12b}	294		3050	2851-2936		1624	1607	1595	
[XI] _{3a}	344	3413	3050	2850-2926		1627	1600	1585	
[XI] _{12a}	287	3379	3070	2851-2924		1630	1601	1580	

تحضير وتشخيص قواعد شف جديدة تحوي على وحدة الاوكسازولين او

البايرازولين

مصطفى سعد خزعل ، جمبد هرمز توما

قسم الكيمياء ، كلية التربية ابن الهيثم ، جامعة بغداد

استلم البحث في : 27 شباط 2011

قبل البحث في : 12 نيسان 2011

الخلاصة

يتضمن هذا البحث تحضير قواعد شف جديدة تحتوي على حلقات غير متجانسة متنوعة مثل أوكسازولين ، بايرازولين باستعمال الجالكون مادة اساسية ، يحضر الجالكون $[II]_{a,b}$ من تفاعل 4-أمينو اسيتوفينون مع بارا-نايتروبنزالديهيد أو بارا-كلوروبنزالديهيد في وسط قاعدي بوساطة تفاعل كلايسين-شمدمت. يتفاعل الجالكون $[II]_{a,b}$ مع هايدروكسيل أمين هايدروكلورايد مؤديا الى تكوين مشتقات الايزوكسازولين $[III]_{a,b}$ ، بينما يؤدي تفاعل أحد أ نواع الجالكونات $[II]_a$ مع الهايدرازين الى تكوين البايرازولين $[III]_a$.

حضرت قواعد شف $[VIII]_n$ - $[IX]_n$ و $[X]_m$ - $[XI]_m$ من تفاعل مركبات حلقيه غير متجانسة مختلفة ؛ أوكسازولين $[III]_{a,b}$ ، بايرازولين $[III]_a$ مع ألديهيدات أحادية $[VI]_n$ و ألديهيدات ثنائية $[VII]_m$ على التوالي في بنزين جاف وقطرات من حامض الخليك الثلجي مع التصعيد العكسي .

شخصت جميع المركبات المحضرة في هذا البحث من خلال قياس درجات أنصهارها فضلا عن الطرائق الطيفية المتمثلة بطيف الأشعة تحت الحمراء، وطيف الأشعة فوق البنفسجية، وطيف الرنين النووي المغناطيسي البروتوني (لبعض منها).

الكلمات المفتاحية : اوكسازولين ، بايرازولين ، قواعد شف