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Synthesis of new Schiff Bases via α,β-unsaturated carbonyl compournds

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Abstract

The synthesis of new Schiff Bases have been achieved by interesting of aldol condensation product of two carbonyl compounds, the products have been treated with thioethane in type of Michael reaction, to produce Michael product, which finally was treated with different aromatic amines to give the Schiff Bases.

These compounds have been characterized by spectroscopic methods (FTIR , HNMR , UV-Vis) , TLC and melting points.

الخلاصة

تم تحضير قواعد شف جديده ، بالاستفادة من تفاعل تكاثف الدول بين مركبي كاربونيل ، وبمعاملة الناتج مع ثايوايثان من خلال تفاعل اضافة مايكل Michael Addition، ومعاملة ناتج اضافة مايكل مع امينات اروماتية مختلفة تم الحصول على قواعد شف .

تم تشخيص المركبات الناتجة بالتقنيات الطيفية (الاشعة تحت الحمراء ، الرنين النووي المغناطيسي، والاشعة فوق البنفسجية المرئية) و درجات الانصهار و كروموتغرافيا الطبقة الرقيقة TLC.

Introduction

The importance of Schiff bases in organic synthesis has increased over the past few decades because they are among the most versatile organic synthetic intermediates (1) and they also present a broad range of biological activities such as herbicidal (2), antifungal (3), antimicrobial (4-7) and antitumor properties (8-9). Moreover, Schiff bases have also attracted much attention because of their ability to act as ligands for complexation of different metal ions in various oxidation states (10-11) .In consideration of these facts , herein we are gratified to report the synthesize some new Schiff bases with expected significant biological activity, which will studied in the future.

Experimental

The melting points were measured on Electrothermal 9300 . The FTIR spectra were recorded on Shimadzu FTIR -8400S spectrophotometer using KBr disc. The UV-Visible spectra were recorded on Shimadzu UV Visible -1650 spectrophotometer . The ^{1}H-NMR spectra were recorded on a Fourier transform Bruker spectrometer operating at 300 MHz in detoured chloroform with tetramethylsilane as internal standard in DMSO- d^6

3-(4-hydroxyphenyl)-1-phenylprop-2-en-1-one (1a):

To a mixture of (0.02 mole, 2.4gm) of acetophenone dissolved in solution of [(0.1 mole, 4gm) sodium hudroxide 20 ml ethanol and 20 ml water], then (0.02 mole , 2.4 gm) of p-hydroxybenzaldehyde was added drop wise with stirring for 30 min. a yellow precipitate was obtained , washed with water,and then recrystallized from ethylacetate-ethanol, table (1 and 2).

3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one (1b):

To a mixture of (0.02 mole, 2.40 gm) of acetophenone dissolved in solution of [(0.1 mole, 4gm) sodium hudroxide 20 ml ethanol and 20 ml water], (0.02 mole , 2.98 gm) of 4-(N,N-dimethylamino) benzaldehyde was added drop wise with stirring for 30 min. a white-yellowish precipitate was obtained , washed with water,and then recrystallized from ethylacetate-diethylether, table (1 and 2).

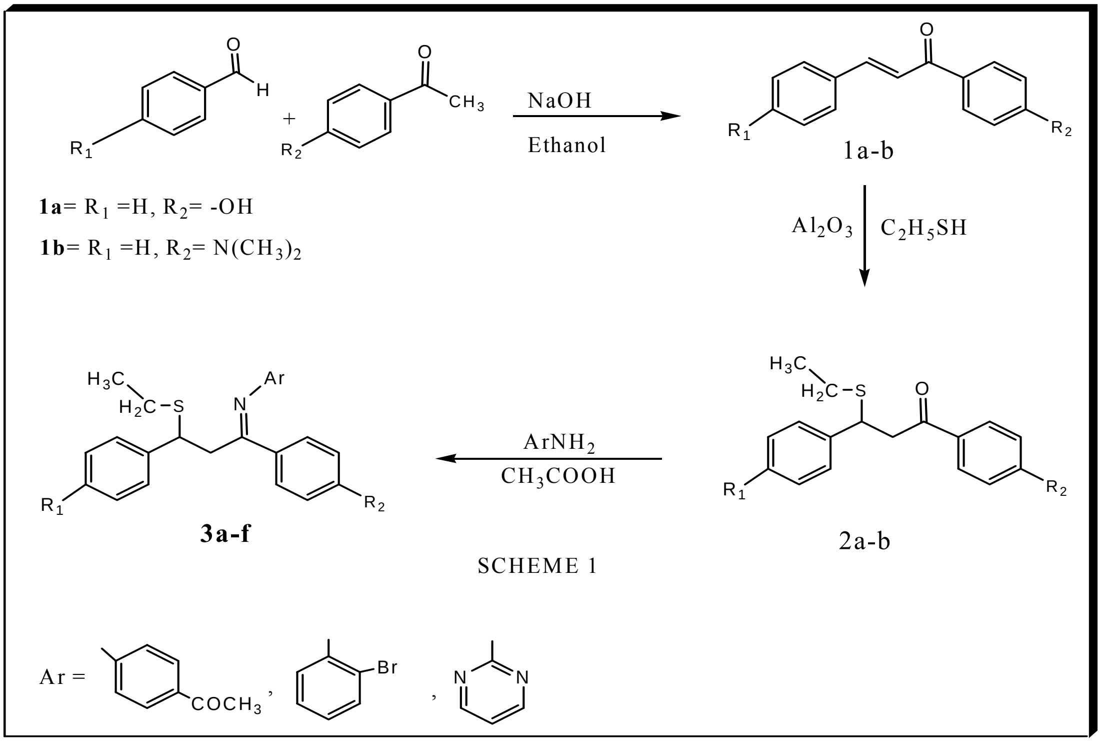
|General procedure

3-aryl -3-ethylthio -1-aryl propan-1-one (2a-b)(12)

To solution of 1-aryl-3-arylprop-2-en-1-one (0.01 mole) dissolved in 20ml absolute methanol , added solution of (0.01 mole) ethylthiol in absolute methanol catalyzed with a catalytic amount of aluminum oxide (Al_2O_3) ,refluxed for 2 hours , the solution was distilled to obtain the precipitate , recrystallized from diethyl ether. Table (1 and 2).

N-(3-aryl-3-(ethylthio)-1-phenylpropylidene)aryl-2-amine(13-14)

To a mixture of 3-aryl -3-ethylthio-1-aryl propan-1-one (0.01 mole) in 25ml ethanol , the aryl amine (0.01 mole) solution in 10ml ethanol, 2-3 drops of glycial acetic acid was added , the mixture was refluxed for 2hours. After the mixture was cooled , the crystals was filtered , washed with water, and then recrystallized from ethanol-water 2:1. Tables (1-2)



SCHEME 1

Results and Discussion

The aim of this work is to synthesize new Schiff bases containing sulfur atom in the beta position to the imine group, via Micheal addition type.

Synthesis of starting materials α,β-unsaturated carbonyl compounds which based on the Aldol condensation of aldehyde and methyl ketone in sodium hydroxide solution afforded compounds 1a-b. Their structures were confirmed by FTIR spectra which show *v* 3100 cm^{-1} (C=C-H), v 1640 cm-1 (C=C),1690-1665 cm^{-1} for (C=O).

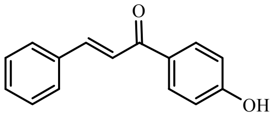
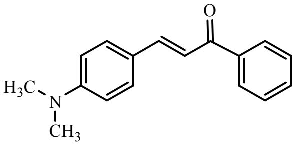
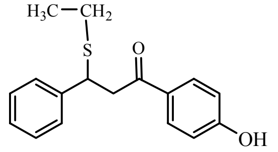
Treatment of α,β-unsaturated carbonyl compounds (1a-1b) with thioethane in Michael type addition catalyzed by aluminum oxide to give β-ethylthio carbonyl compounds (2a-b), Their structures were confirmed by FTIR spectra which show the absence of the peak near 3100 cm^{-1} for (C=C-H), 1640 cm-1 for (C=C) and appear a new peak near 2960 and 2870 cm^{-1} for (CH_3,CH_2) , 1690-1665 cm^{-1} for (C=O).

Finally treatment of ethylthio carbonyl compounds (2a-b) with different aromatic amines (2-aminopyrimidine, 4-aminoacetophenone and 2-bromoaniline) gives new Schiff bases (3a-f) , the structures were determined by FTIR spectra which show the absence of C=O stretching vibration in the region (1695-1665 cm^{-1}) and appear a new peak in the region 1630-1595 cm^{-1} according to stretching vibration for (C=N) bond.

The 1HNMR of compound [4-(3-(ethylthio)-3-phenyl-1-(pyrimidin-2-ylimino)propyl)phenol] (Fig. 1)show multiple peaks at δ ppm 8.3,8.2 and 7.5 for 3H (pyrimidine protons), 4H multiplet for aromatic protons (7.2-6.6) ,3.75 for (OH) , 1H triplet (3.4,3.2)for (CH) .and 2H doublet (1.4,1.2) for (CH_2).(15)

Physical and spectral data are listed in table (1 and 2).

Table (1) Physical Data of Prepared Compounds

Comp. no.	structure	m.p. ^{o}C	Colour	Yield %
1a	 1-(4-hydroxyphenyl)-3-phenylprop-2-en-1-one	224-226	Redish brown	82%
1b	 3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one	251-253	Greenish yelow	79%
2a	 3-(ethylthio)-1-(4-hydroxyphenyl)-3-phenylpropan-1-one	284-286	Yellowish orange	77%

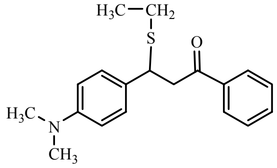
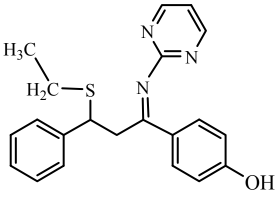
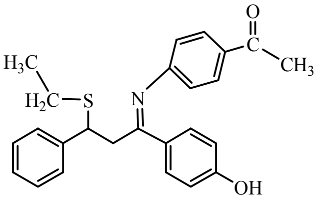
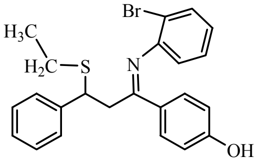
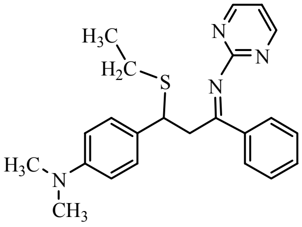
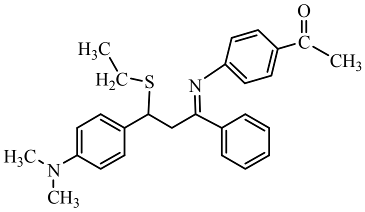
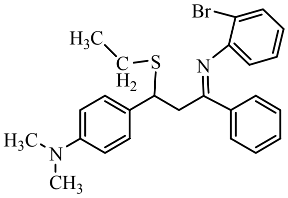
2b	 3-(4-(dimethylamino)phenyl)-3-(ethylthio)-1-phenylpropan-1-one	313-314	yellow	71%
3a	 4-(3-(ethylthio)-3-phenyl-1-(pyrimidin-2-ylimino)propyl)phenol	363-364	Orange	72%
3b	 1-(4-(3-(ethylthio)-1-(4-hydroxyphenyl)-3-phenylpropylideneamino)phenyl)ethanone	290-292	Red	66%
3c	 4-(1-(2-bromophenylimino)-3-(ethylthio)-3-phenylpropyl)phenol	223-225	Yellow greenish	91%
3d	 *N*-(3-(4-(dimethylamino)phenyl)-3-(ethylthio)-1-phenylpropylidene)pyrimidin-2-amine	61-63	Green	76%
3e	 1-(4-(3-(4-(dimethylamino)phenyl)-3-(ethylthio)-1-phenylpropylideneamino)phenyl)ethanone	Decom. 244	Redish yellow	58%
3f	 2-bromo-*N*-(3-(4-(dimethylamino)phenyl)-3-(ethylthio)-1-phenylpropylidene)benzenamine	250-253	Green	65%

Table (2) Spectral Data of Prepared Compounds

Comp. no.	λmax EtOH	IR *v* cm^{-1} KBr disc					1HNMR δ(ppm) $DMSO-d_6$
		O-H	C=C-H	C=O	C=N	C=C alph.	
1a	450	3500-3400		1685		1640	
1b	460			1675		1645	
2a	455	3500-3400	3100	1680			
2b	470		3095	1665			
3a	385	3500-3500			1595		δ(OHal.,3.75),δ(C-Hal.3.4 and 1.4),δ(C-Har.,7.2,6.80.6.6),δ(C-Hhet.(8.3,8.2,7.4)
3b	370	3500-3500			1610		
3c	395	3500-3500			1615		
3d	407				1620		
3e	410				1630		
3f	430				1625		

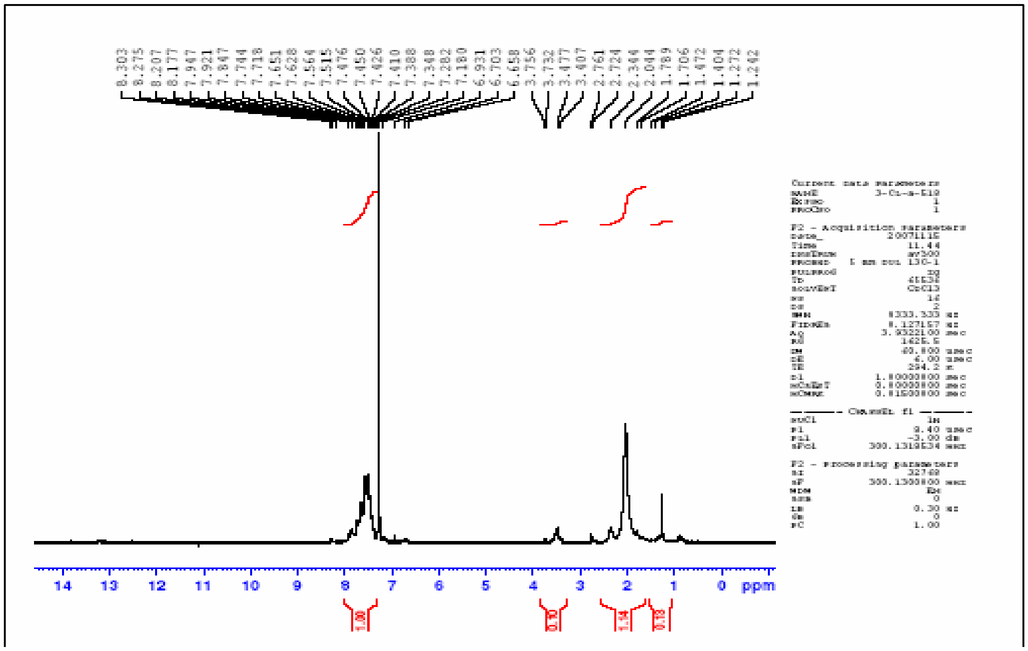


Fig. 1: The ^{1}HNMR of compound [4-(3-(ethylthio)-3-phenyl-1-(pyrimidin-2-ylimino)propyl) phenol]

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