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Antifungal Activities of Ketoazomethines of Phenyl Glyoxal and *p*-Substituted Anilines

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Abstract: A new series of ketoazomethines were synthesized by condensation of phenyl glyoxal (prepared by partial oxidation of acetophenone) with various *p*-substituted anilines *viz.* *p*-Cl, *p*-Br, *p*-NO_2, *p*-$(C_2H_5)_2N$ and *p*-CH_3. These compounds were characterized by elemental analysis, IR and H^1 NMR. The synthesized ketoazomethines were screened for their antifungal activity against hazardous fungi namely *Fusarium oxysporum, Alternaria brassicola, Sclerotium* and *Pythium.*

Keywords: Ketazomethines, Synthesis, Antifungal activity.

Introduction

Schiff's bases and their complexes obtained by reactions with transition metals[1] are well known for their antibacterial[2, 3], antineoplastic[4], antiviral[5], anti-inflammatory[6,7] activity and are used to design medicinal compounds[8-10]. Many researchers studied the synthesis[11-12], characterization and structure activity relationship of Schiff's bases[13-17]. The present study includes synthesis of a new series of ketoazomethines obtained by condensation of phenyl glyoxal with *p*-substituted anilines *viz.* *p*-Cl, *p*-Br, *p*-NO_2 *etc.* and examine their antifungal activity against hazardous fungi *i.e. Fusarium oxysporum, Alternaria brasssicola, Sclerotium* and *Pythium* which causes harm to crops like tomato, onion, cauliflower, broccoli *etc*.

Experimental

All the chemicals used were either E-Merck or Qualigens. Melting points of all the compounds determined in open glass capillaries were uncorrected. Elemental analysis of samples was carried out on Euro EA elemental analyzer. Infrared spectra were recorded in

KBr medium on Thermo Nicollet Nexus FT-IR spectrophotometer and 300MHz NMR spectra were recorded in dimethylsulphoxide medium on Varian C-13 NMR spectrometer using TMS as internal standard. Column chromatography was carried out using silica gel (finer than 200#).Characterization data is presented in Table 1 and spectral data in Table 2**.**

Table 1. Physical characteristics and elemental analysis of ketoazomethines

Compd	M.F	Color	M P ^{0}C	Analysis					
				C %		H %		N%	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
4A	$C_{14}H_{10}NOCl$	Light pink	151	68.85	68.65	4.09	4.01	5.73	5.34
4B	$C_{14}H_{10}NOBr$	Pale yellow	163	58.33	58.29	3.47	3.16	4.86	5.10
4C	$C_{14}H_{10}N_2O_3$	Green	187	66.14	66.12	3.93	3.92	11.02	11.1
4D	$C_{14}H_{11}NO$	Light brown	170	80.38	80.20	5.26	4.81	6.69	6.80
4E	$C_{14}H_{15}N_2O$	Scarlet Red	161	77.14	77.67	7.14	7.31	10.00	9.84
4F	$C_{15}H_{13}NO$	Brown	180	80.71	80.60	5.82	6.08	6.27	6.23

Table 2. Spectral data of ketoazomethines

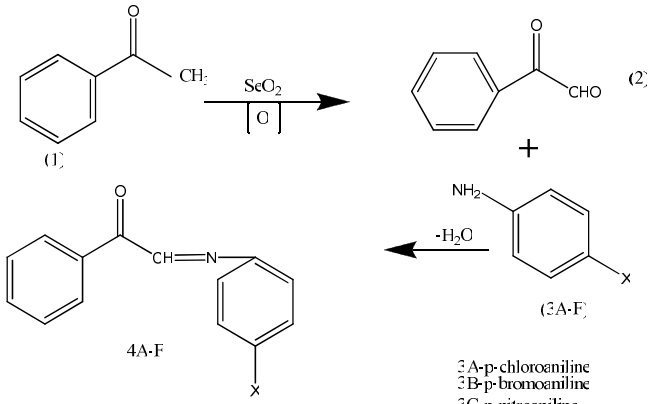
Compd.	νC=O chain	Benzene ring		νC=N	δC–H (2H)	δC–H (5H)	Subs. Gps freq.	NMR (300 MHz)
		νC–H	νC=C					
$C_{14}H_{10}NOCl$	1626	3012	1475	1646 br	825	696	608 (νC–Cl)	δ2.5(d,2H), δ6.51(s,5HAr-H), δ3.38(s,1H,CH-N),δ6.44(s,4H,Ar H),δ1.12(3H,CH_3)
$C_{14}H_{10}NOBr$	1671	3023	1494	1589	811	780	502	
$C_{14}H_{10}N_2O_3$	1634	2990	1476	1590	838	753, 696	1304, 1578 νC–NO_2)	
$C_{14}H_{11}NO$	1670	3055	1498, 1444	1593	-	755, 695	-	
$C_{14}H_{15}NO$	1672	3074	1510, 1453	1593	815	752, 688	1453 (δCH_2), 1354 (δCH_3)	
$C_{15}H_{13}NO$	1630	3029	1560, 1479	1560	826	709	1357(δCH_3)	

Preparation of phenyl glyoxal

Phenyl glyoxal was prepared by the partial oxidation of acetophenone with selenium dioxide. Reaction mixture containing acetophenone (0.1 mol,1) and selenium dioxide (0.1 mol) in round bottom flask containing 95% ethyl alcohol was refluxed for 4-6 h. Orange yellow reaction mixture was decanted and concentrated over water bath and dissolved in ether to remove selenium from the product.

*Preparation of ketoazomethines(**4a-f**) (Scheme 1)*

Phenyl glyoxal (2, 0.2 mol) and aniline (3A-F, 0.2 mol) were taken in a round bottom flask containing 100 mL of ethanol and refluxed on water bath for 8 h. Excess of ethanol was removed from reaction mixture and cooled at room temperature. Then it was poured in ice cold water and filtered. Solid obtained were collected and recrystallized with ethanol.



Scheme 1

Antifungal activities

Preparation of medium and sample solutions

For the preparation of PDA (Potato Dextrose Agar) medium 250 g potato pieces boiled in water were filtered and filtrate was made up to 1 liter**.** To this solution 20 g dextrose powder was added followed by heating to a syrupy viscous consistency. Standard solutions of all the samples of 50 ppm concentration were prepared by dissolving known quantity of compounds in known volume of DMSO (dimethylsulphoxide).

Antifungal activities were performed by paper disc method[18]. First of all PDA medium was sterilized in Autoclave and then poured into autoclaved Petri dishes near the gas flame, to avoid contamination and these plates were placed in Laminar Air Flow for an hour. There after filter paper discs dipped in sample solution were placed on medium in Petri dish and kept in Laminar Air Flow for half an hour. Fungus bit of 1mm diameter was put at a distance of 1 cm from paper disk wet in sample solution and Petri dishes were sealed with paraffin film in incubator at 25-30 ^{0}C for 72-96 h for growth of fungus. Fungal growth was measured as the mean of distances from inoculation point of fungus to its maximum growth in three directions. Three replicates were used for each fungus.

The synthesized compounds were subjected to antifungal screening and compared against a standard fungicide Diethane M-45 and DMSO as control with no inhibition; results are given in Table 3.

Table 3. Results of inhibition of synthesized ketoazomethines

Compd.	Inhibition. Time, days	S	P	F.O.	A. B.
$C_{14}H_{11}NO$	3	++	+	+	+
$C_{14}H_{10}NOBr$	3	++	++	+	++
$C_{14}H_{10}NOCl$	3	++	+	++	++
$C_{14}H_{10}N_2O_3$	3	+	++	++	++
$C_{15}H_{13}NO$	3	+	-	-	-
$C_{14}H_{15}N_2O$	3	-	+	-	-
Diethane-M45	3	-	-	+	+

S.- Sclerotium, P.-Pythium, A.B. -Alternaria Brassicola, F.O.-Fusarium Oxysporum, -Ve-1-7mm, +Ve-7-14mm, ++Ve-15-20 mm

Results and Discussion

The antifungal studies of the compounds were tested by paper bit method against hazardous fungi namely *Fusarium Oxysporum, Alternaria Brassicola, Pythium and Sclerotium* and were compared to reference fungicide Diethane-M45, *p*-chloroanil showed highest inhibition against *Fusarium oxysporum, Sclerotium* and *Alternaria brassicola*, *p*-bromoanil was effective against *Pythium, Sclerotium* and *Alternaria brassicola* while phenylanil was effective against *Sclerotium*, *p*-nitroanil was effective against *Pythium, Alternaria brassicola and Fusarium oxysporum.*

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