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SYNTHESIS OF SUBSTITUTED-4, 6-DIARYL-2-IMINO-PHENYL-3HYDRO-1, 3-THIAZINE

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ABSTRACT

Six different chalcones **Ia – If** were synthesized by condensing 2-hydroxy-3-iodo-5-methyl acetophenone with six different aromatic aldehydes in ethanol using NaOH. These chalcone were cyclized with phenyl thiourea in ethanol yielding **IIa – IIf**. The synthesized compounds were characterized by I.R., NMR spectral analysis.

Key words: Substituted 4, 6-diaryl-2-imino-phenyl-3hydro-1, 3-thiazine.

INTRODUCTION

Koketsu et al.[1,2] have synthesized 1, 3-thiazine derivatives, a potential antimicrobial agents and also synthesized 2-alkyl thio-1,3-thiazine derivatives from s- alkyldithiocarbamate and α, β-unsaturated ketone. Fisyuk[3] have synthesized with new approach for 1,3-chloro-isothiocynatoalkanes and synthesis of tetrahydro-1,3-thiazine-2-thiones and 2-alkylamino-5,6-dihydro-1,3-thiazines. Montis et al.[4] have synthesized high yield 4H-1,4-benzo-thiazine-dioxide derivative. Yuskovets et al.[5] have synthesized new method for synthesis of 5-acyl-1,3-thiazines.

Leflemme et al.[6] have synthesized dihydro and tetrahydro-1,3-thiazine derivatives from β aryl-β-amino acid. Koketsu et al.[7] synthesized 4-etyl-4-hydroxy-2-phenyl-5, 6-dihydro-4H-1,3-thiazine. Lin[8] have synthesized metyl-2-amino-4-metyl-6-phenyl 6H-1,3-thiazine-5-carboxylate Koketsu et al.[9] have synthesized 4-hydroxy-4-metyl-2, 6-diphenyl-5, 6-dihydro-4-H-1, 3-thiazine. Nagrajan et al.[10] have synthesized and studied biological activity of bis-chalcones, bis-thiazines, and bis-pyrimidines.

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Muraoka et al.[11,12] have synthesized 1, 3-thiazines-2, 6-dithiones and 2-alkylthio-2,3-dihydro-1, 3-thiazine-6-thiones by reductive alkylation of 1, 3-thiazine-2, 6-dithiones and also synthesized 1, 3-thiazine derivatives from 2-iminocyclopentanedithiocaboxilic acid. Kimpe and Rocchetti[13] have synthesized 5-acetyl-2,3-dihydro-1,4-thiazine, a very intense roasty, popcorn like odorant. Ingarsal et al.[14] have synthesized and antimicrobial activity of some amino-4-[1,1'-biphenyl-4-yl]-6-aryl-6H-1,3-thiazines.

EXPERIMENTAL

Melting points of all synthesized compounds were determined in open capillary tube and are uncorrected. The purity of compounds were checked by TLC using silica G. I. R. spectra were recorded on Perkin-Climer-841 spectrometer (cm^{-1}) in KBr disc and NMR (Brucker Avance II 400 NMR) using $CDCl_3$ as solvent.

Synthesis of 2-hydroxy-3-iodo-5-methyl-acetophenone (Compound-I)

By known method from p-cresol to p-crysyl-acetate prepared and then by fries migration-2-hydroxy-5-methyl acetophenone which on iodination gives 2-hydroxy-3-iodo-5-methyl acetophenone (Comp.-I).

Characterization data of compound

2-hydroxy-3-iodo-5-metyl acetophenone (I)

IR (KBr) ν_{max} cm^{-1}

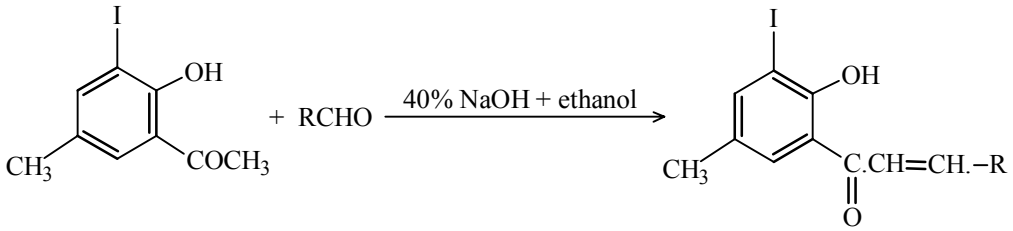
Absorptions observed in cm^{-1}	Intensity	Assignment
3200	s	Phenolic OH
2919	s	Ar-C-H Streaching
1635	s	C=O streaching
1082-1007	s	CH_3 streaching
1020	s	CH_3 streaching
550	s	C-I streaching

^{1}H NMR: [δ $CDCl_3$]

Chemical shift in δ	Nature of peak (Multiplicity)	No. of protons	Type of protons
2.3	s	3H	Ar-CH_3
2.6	s	3H	$COCH_3$
7.5	s	1H	Ar-H
7.7	s	1H	Ar-H
12.9	br	1H	Ar-OH

Synthesis of substituted 2-hydroxy-3-iodo-5-methyl chalcones [Ia – If]

Compounds **Ia** to **If** were synthesized from 2-hydroxy-3-iodo-5-methyl acetophenone by reacting with six different aromatic aldehydes by known method in solvent ethanol using 40% NaOH. The physical data of compound **Ia** to **If** is given in Table 1.

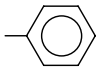
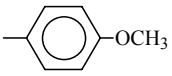
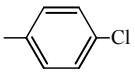


(I) **Ia - If**

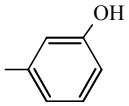
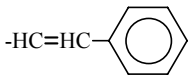
Scheme 1

The groups R are shown in Table 1.

Table 1: Physical data of compound Ia - If

Compound	R	Mole. Formula	M.P. (^{o}C)	Yield
Ia		$C_{16}H_{13}O_2I$	110^{o}C	72%
Ib		$C_{17}H_{15}O_3I$	142^{o}C	68%
Ic		$C_{16}H_{12}O_2ICl$	160^{o}C	70%

Cont…

Compound	R	Mole. Formula	M.P. (^oC)	Yield
Id		$C_{16}H_{13}O_3I$	80^oC	66%
Ie		$C_{18}H_{15}O_2I$	130^oC	63%
If		$C_{14}H_{11}O_3I$	80^oC	65%

Characterization data of compound

Synthesis of 2-hydroxy-3-iodo-5-methyl-phenyl)-4-methoxy chalcone (Ib)

IR (KBr) ν_{max} cm^{-1}

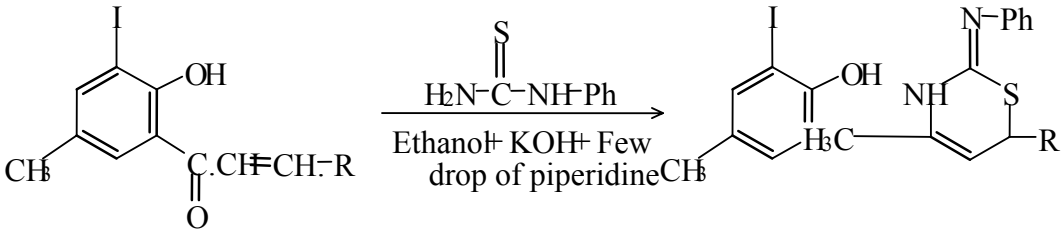
Absorptions observed in cm^{-1}	Intensity	Assignment
3412	br	Phenolic OH
2912	s	AR-C-H- Stretching
1743	s	C=O stretching
1637-1604	s	O=C-CH=CH
1352	s	C-O stretching in Phenol
1266-1237	s	Ar-O stretching in ether
821.12	s	C-I stretching

^{1}H NMR: [$CDCl_3$]

Chemical shift (δ)	Nature of peak (Multiplicity)	No. of protons	Type of protons
2.31	s	3H	Ar-CH_3
3.85	s	3H	O-CH_3
6.9	d	2H	-CH=CH
7.2-8.1	m	6H	Ar-H
13.7	s	1H	Phenolic OH

Synthesis of substituted 4,6-diaryl -2-imino phenyl-3- hydro-6H-1,3-thiazine (IIa-IIf)

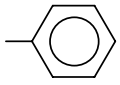
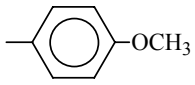
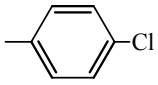
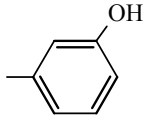
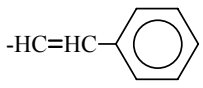
Compound (**Ia** to **If**) 0.01 M and phenyl thiourea 0.01 M and 0.02 M KOH solution with a few drops of piperidine were refluxed in 25 mL ethanol for 2 to 2.5 hours. Dilute it with water and acidified with conc. HCl. The product crystallized from ethanol. Physical data are shown in Table 2.



(Ia - If) **(IIa - IIf)**

Scheme 2

Table 2: Physical data of compound IIa - IIf

Compound	R	Mol. Formula	M.P. (^{0}C)	Yield
IIa		$C_{23}H_{19}ON_2S$ I	110^{o}C	65%
IIb		$C_{24}H_{21}O_2N_2S$ I	130^{o}C	60%
IIc		$C_{23}H_{18}ON_2S$ I Cl	120-124^{o}C	62%
IId		$C_{23}H_{19}O_2N_2S$ I	148^{o}C	63%
IIe		$C_{25}H_{21}ON_2S$ I	160^{o}C	58%
IIf		$C_{21}H_{17}O_2N_2S$ I	98-102^{o}C	60%

Characterization data of compound-4-(2'-hydroxy-3-iodo-5-methyl phenyl)-6-(4-methoxy phenyl)-imino-2-phenyl-3-hydro-6H-1, 3-thiazine (IIb)

IR (KBr) ν_{max} cm^{-1}

Absorptions observed in cm^{-1}	Intensity	Assignment
3206	br	O-H streaching in phenol
2914	s	N-H streaching
2836	s	Ar-H streaching
1691	s	C=C streaching vibration in aryl group
1235	s	C-N streaching
1258	s	Ar-O streaching
694	s	C-I stretching

^{1}H NMR: [$CDCl_3$]

Chemical shift (δ)	Nature of peak (Multiplicity)	No. of protons	Type of protons
2.1-2.6	s	3H	Ar-CH_3
2.8-3.1	q	2H	CH_A and CH_B
3.8-4.0	s	3H	OCH_3
5.5	d	1H	-N-H
6.7-8.6p	m	11H	Ar-H
13.8	s	1H	Ar-OH

RESULTS AND DISCUSSION

Compound **Ia – If** and **IIa – IIf** were synthesized through the route as shown in general reactions R and R**'** as shown in Table 1 and 2. Similarly, physical data are shown in Tables 1 and 2. The synthesized compounds **Ib** and **IIb** were confirmed on the basis of IR and NMR spectral analysis.

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