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SYNTHESIS OF SUBSTITUTED-4, 6-DIARYL-2-IMINO-6H-2, 3-DIHYDRO-1, 3-THIAZINE

A. S. DIGHADE* and S. R. DIGHADE

Department of Chemistry, Bar. R. D. I. K. & N. K. D College, BADNERA (M.S.) INDIA

ABSTRACT

Six different chalcones $\mathbf{I_a}$-$\mathbf{I_f}$ 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 thiourea in ethanol yielding **IIa – $\mathbf{II_f}$**. The synthesized compounds were characterized by I.R., NMR spectral analysis.

Key words: Substituted iodo- 1, 3-Thiazine.

INTRODUCTION

Nagrajan and Reddy[1] have synthesized and studied biological activity of bis-chalcones, bis-thiazines, bis-pyrimidines. Muraoka et al.[2], have synthesized reaction of 1, 3-thiazines-2, 6-dithiones and synthesis of 2-alkylthio-2, 3-dihydro-1, 3-thiazine-6-thiones by reductive alkylation of 1, 3-thiazine-2, 6-dithiones. Koketsu et al.[3], have synthesized 4-hydroxy-4-metyl-2, 6-diphenyl-5 5, 6-dihydro-4-H-1, 3-thiazine. Muraoka et al.[4] synthesized 1, 3-thiazine derivatives from 2-iminocyclopentanedithiocaboxilic acid. Koketsu et al.[5] synthesized 4-etyl-4-hydroxy-2-phenyl-5, 6-dihydro-4H-1, 3-thiazine[5].

Lin[6] has synthesized metyl-2-amino-4-metyl-6-phenyl 6H-1, 3-tiazine-5-carboxylate. Kimpe and Rocchetti[7] have synthesized 5-acetyl-2, 3-dihydro-1, 4-thiazine, a very intence roasty, popcornlike odorant. Yuskovets et al.[8] have synthesized new method for synthesis of 5-acyl-1, 3-thiazines. Leflemme et al.[9] have synthesized dihydro and tetrahydro-1, 3-thiazine derivatives from β aryl-β-amino acid. De Montis et al.[10] have synthesized high yield 4H-1, 4-benzo-thiazine-dioxide derivative. Fisyuk et al.[11] have synthesized 1,3 chloroisothiocynato alkanes, tetrahydro-1, 3-thiazine-2-thiones and 2-alkylamino-5, 6-dihydro-1, 3-thiazines with new approach[11].

*Author for correspondence; E-mail: aprana_dighade@rediffmail.com

EXPERIMENTAL

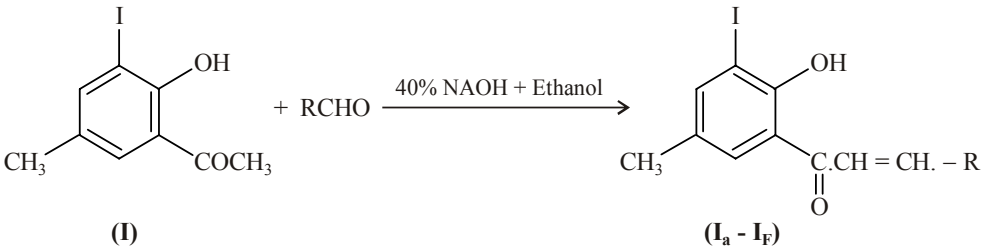
Melting points of all synthesized compounds were determined in open capillary tube and are uncorrected. The purity of compounds were checked by TLC using silica G. I. R. spectra were recorded on Perkin-Climer-841 spectrometer (cm^{-1}) in KBr disc and NMR (Brucker Avance II 400 NMR) using $CDCl_3$ as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

Synthesis of 2-hydroxy-3-iodo-5-methyl-acetophenone (Compound-1)

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.-1).

Synthesis of substituted 2-hydroxy-3-iodo-5-methyl chalcones [I_a – I_f]

Compounds **I_a** to **I_f** 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 compounds **I_a** to **I_f** is given in Table 1.

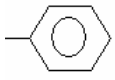
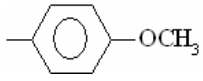


(I) **(I_a - I_F)**

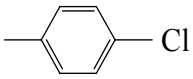
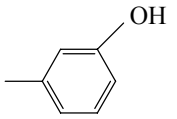
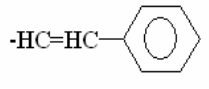
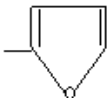
Reaction Scheme 1

The groups R are shown in Table 1.

Table 1: Physical data of I_a – I_f

S. No.	Compd. No.	R	Mole. formula	M.P. (^oC)	Yield (%)
1.	I_a		$C_{16}H_{13}O_2I$	110^oC	72%
2.	I_b		$C_{17}H_{15}O_3I$	142^oC	68%

Cont…

S. No.	Compd. No.	R	Mole. formula	M.P. (^oC)	Yield (%)
3.	I_c		$C_{16}H_{12}O_2ICl$	160^oC	70%
4.	I_d		$C_{16}H_{13}O_3I$	80^oC	66%
5.	I_e		$C_{18}H_{15}O_2I$	130^oC	63%
6.	I_f		$C_{14}H_{11}O_3I$	80^oC	65%

Characterization data of compound

2-Hydroxy-3-iodo-5-metyl acetophenone

IR (KBr) ν_{max} cm^{-1}: 3200 cm^{-1} (s) – phenolic OH , 2919 cm^{-1} (s) – Ar- C-H stretching, 1635 cm^{-1} C = O stretching, 1082-1007 cm^{-1} (S) CH_3 - stretching , 1020 cm^{-1} (S) CH_3 stretching, 550 cm^{-1} C-I stretching.

^{1}H NMR: [δ $CDCl_3$]: 2.3 δ (S, 3H, Ar- CH_3), 2.6 δ (S, 3H, $COCH_3$), 7.5 δ (S, 1H, Ar-H), 7.7 δ (S, 1H, Ar-H), 12.9 δ (S, 1H, Ar-OH).

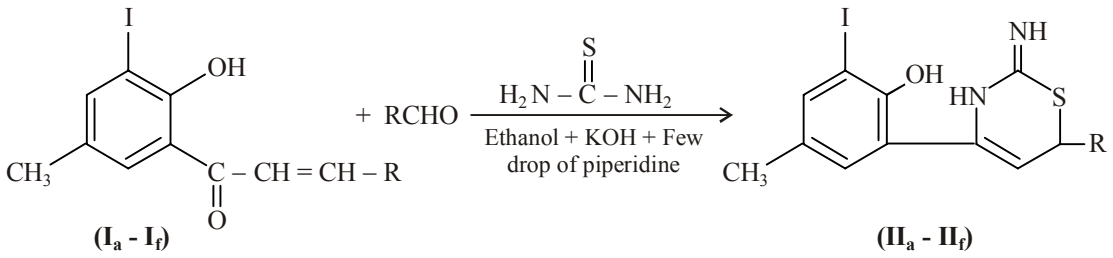
1-(2-hydroxy-3-iodo-5-methyl benzoyl)- 4- phenyl-1, 3-butadine

IR (KBr) ν_{max} cm^{-1}: 3400 cm^{-1} (br) – phenolic OH, 2914 cm^{-1} (s) – Ar- CH stretching, 1631cm^{-1} O = C-CH = C stretching, 1353 cm^{-1} (S) C-O stretching in Phenol, 1230 cm^{-1} Ar-O stretching in ether, 552 cm^{-1} C-I stretching .

^{1}H NMR: [δ $CDCl_3$]: 2.1-2.3δ (S, 3H, Ar- CH_3), 2.8-3.0 δ (m, 1H, O = C-CH = C), 5.2-5.3 δ (m, 2H, -CH = CH), 6.8-7.8 δ (Ar-CH = CH (2H) & (7H, Ar-H), 13.5-13.6 δ (S, 1H, Ar-OH).

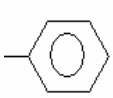
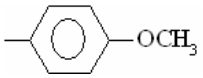
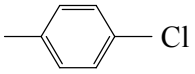
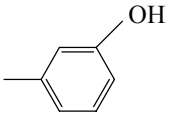
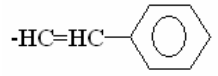
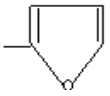
Synthesis of substituted 4, 6-diaryl -2-imino-6H-2, 3-hydro- 1, 3-thiazine

Compound ($I_{(a)}$ to $I_{(f)}$) 0.01 M, 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 products were crystallized from ethanol. Physical data are shown in Table 2.



Reaction Scheme 2

Table 2: Physical data of II_a – II_f

S. No.	Compd. No.	R	Mole. formula	M.P. (^oC)	Yield (%)
1.	II_a		$C_{17}H_{15}ON_2S$ I	74^{o}C	65%
2.	II_b		$C_{18}H_{17}O_2N_2S$ I	110^{o}C	60%
3.	II_c		$C_{17}H_{14}ON_2S$ I Cl	124^{o}C	62%
4.	II_d		$C_{17}H_{15}O_2N_2S$ I	86^{o}C	63%
5.	II_e		$C_{19}H_{17}ON_2S$ I	150^{o}C	58%
6.	II_f		$C_{15}H_{13}O_2N_2S$ I	90^{o}C	60%

Characterization data of compound

4-(2-hydroxy-3-iodo-5-methylphenyl)-6-(2-phenyl-ethenyl)-2-imino-6-H-2,3-dihydro 1,3-thiazine

IR (KBr) ν_{max} cm^{-1}: 3378 cm^{-1} (br) Ar-OH, 3055 cm^{-1} (S) – C-N-H- stretching, 3023 cm^{-1} (s) C = N-H stretching, 2919 cm^{-1} (s) CH stretching IN aliphatic CH_3, 1341 cm^{-1} C-N-H stretching, 1239 cm^{-1} Ar-O stretching in, 555 cm^{-1} C-I stretching.

^{1}H NMR: [δ $CDCl_3$]: 2.3 δ (S, 3H, Ar- CH_3), 2.5-2.6 (d, 1H, CH -A), 3.5 (d, 1H, CH –B), 4.1 (S, 1H, = N-H), 6.5-8.1 (m, 7H-Ar-H) & (Ar-CH = CH, 2H) 12.6 - 13.8 (1H, Ar-OH).

RESULTS AND DISCUSSION

Compound $\mathbf{I_a - I_f}$ and $\mathbf{II_a - II_f}$ were synthesized through the route as shown in general reactions with R and R' as shown in Table 1 and 2. Physical data are given in Table 1 and 2. The synthesized compounds $\mathbf{I_e}$ and $\mathbf{II_e}$ were confirmed on the basis of IR, NMR spectral analysis.

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