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Synthesis of substituted-4, 6-diaryl-2-imino-diphenyl-6*H*-1, 3-thiazines

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ABSTRACT

Six different Chalcones I(a)-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 diphenyl thiourea in ethanol yielding IIa – II_f . The synthesized compounds were characterized by I.R., NMR spectral analysis.

Key Words: - substituted 4, 6-diaryl-2-imino- diphenyl-6H-1, 3- Thiazines.

INTRODUCTION

M.Koketsu *et al.* have synthesized 1, 3 – thiazine derivatives a potential antimicrobial agents [1] M.Koketsu *et al.* have synthesized 2-alkylthio-1, 3-thiazine derivatives from s- alkyldithiocarbamate and α, β- unsaturated ketone [2]. Nicolas Leflemme *et al.* have synthesized dihydro and tetrahydro-1, 3- Thiazine derivatives from β aryl – β- amino acids [3]. X.F.Lin has synthesized metyl-2-amino-4-metyl-6-phenyl 6H-1, 3-Tiazine-5-carboxylate [4]. Stefanie De Montis *et al*. have synthesized high yield 4H-1, 4- benzo- thiazine- dioxide derivative [5]. Fisyuk A.S. have synthesized with new approach for 1, 3 chloroisothiocynatoalkanes and synthesis of tetrahydro-1, 3-thiazine-2-thiones and 2- alkylamino -5, 6- dihydro-1, 3-thiazines [6]. V.N.Yuskovets *et al* have synthesized new method for synthesis of 5-acyl-1, 3-Thiazines [7].

M.Koketsu synthesized 4-etyl-4-hydroxy-2-phenyl-5, 6-dihydro-4H-1, 3-thiazine [8]. Norbert G. De Kimpe have synthesized 5-Acetyl-2, 3- dihydro-1, 4- thiazine, avery intense roasty, popcornlike odorant [9]. M.Koketsu *et al*. have synthesized 4-hydroxy-4- methyl-2, 6-diphenyl-5, 6- dihydro-4-H-1, 3- thiazine [10].

Motomu muraoka *et al*. have studied 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 [11]. Motomu Muraoka synthesized 1, 3- thiazine derivatives from 2-iminocyclopentanedithiocaboxilic acid [12]. N.Ingarsal have synthesized and antimicrobial activity of some amino-4-[1, 1'-biphenyl-4-yl] -6-aryl-6H-1,3-thiazines [13].Dipti R.Patil *et al.* synthesized ecofriendly synthesis of benzoxazines and benzothiazines at ambient temperature without catalyst and their antibacterial and antifungal activity [14]. A.Nagrajan *et al*. have synthesized and studied biological activity of bis- Chalcones, bis-Thiazines, and bis-Pyrimidines [15].

Ujwala Sawarkar *at al* has studied synthesis, characterization and antimicrobial activity of some 2-(propen-1-one) aryl-3-substituted phenothiazine [16]. M.S.A.EL-Gaby have studied the synthesis of new cyclopenta [d] [1, 3] thiazine derivative and their use as antimicrobial agent [17]. Ibadur R.Siddique *et al* have studied novel one-pot synthesis of 1, 3-dithiins and 1,3-thiazines under microwave irradiation [18]. Naresh Kumar *et al* have studied

synthesis of some new 10H- pyrido [3, 2-b] [1, 4] banzothiazine and their ribofuranosides as possible chemotherapeutic agents [19].

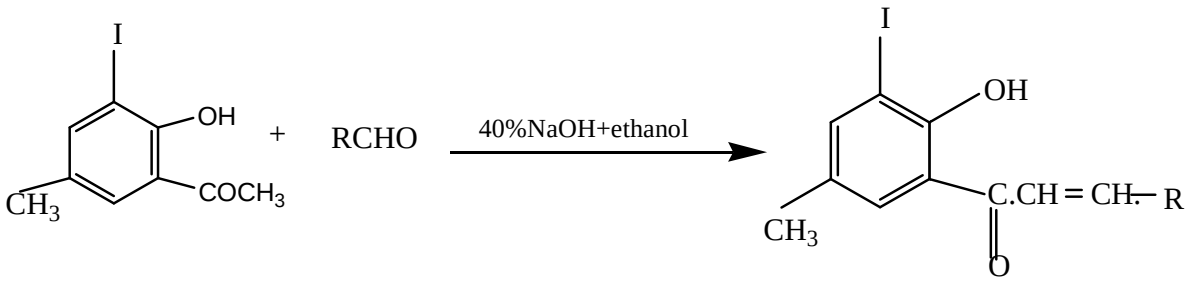
MATERIALS AND METHODS

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).

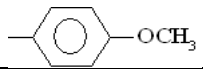
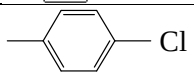
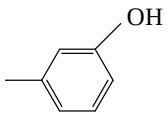
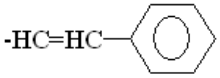
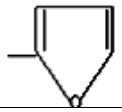
Synthesis of substituted 2-hydroxy-3-iodo-5-methyl chalcones [$I_{(a)} – I_{(f)}$]
Compound $I_{(a)}$to $I_{(f)}$were synthesized from 2-hydroxy-3-iodo-5-methyl acetophenone by reacting with six different aromatic aldehydes by known method in solvent ethanol using 40% NaOH. The physical data of compound $I_{(a)}$ to $I_{(f)}$ is given in table no. 1.

Reaction scheme 1



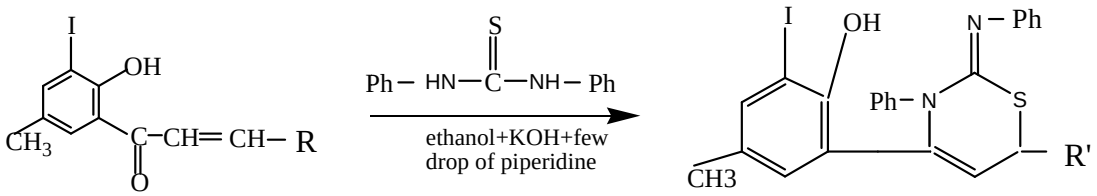
(I) **(Ia – IF)**

The groups R are shown in Table no. 1
Table no.1

S. N.	Compound No.	R	Mole. Formula	M.P.^{0}C	Yield
1.	I_a		$C_{16}H_{13}O_2I$	110 ^{0}C	72%
2.	I_b		$C_{17}H_{15}O_3I$	142 ^{0}C	68%
3.	I_c		$C_{16}H_{12}O_2ICl$	160 ^{0}C	70%
4.	I_d		$C_{16}H_{13}O_3I$	80 ^{0}C	66%
5.	I_e		$C_{18}H_{15}O_2I$	130 ^{0}C	63%
6.	I_f		$C_{14}H_{11}O_3I$	80 ^{0}C	65%

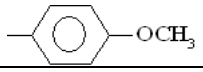
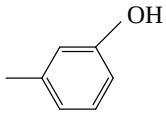
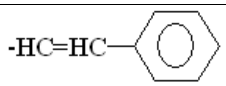
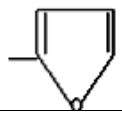
Synthesis of-4,6-diaryl-2-imino-2,3-diphenyl-6H- 1, 3-thiazine. (II_a-II_f)
Compound ($I_{(a)}$to $I_{(f)}$) 0.01 M and diphenyl thiourea 0.01 M and 0.02 M KOH sol^n with a few drops of piperidine were refluxed in 25 ml ethanol for 2 to 2.5 hours. Dilute it with water and acidified with conc. HCL. The product crystallized from ethanol. Physical data are shown in table no. 2.

Reaction scheme no. 2



(I a – I f) **(II a –II f)**

The groups R are shown in Table no.2.

S. N.	Compound No.	R'	Mole. Formula	M.P.^{0}C	Yield
1.	II_a		$C_{29}H_{23}ON_2S$ I	116°C	65%
2.	II_b		$C_{30}H_{25}O_2N_2S$ I	138-142°C	60%
3.	II_c		$C_{29}H_{22}ON_2S$ I Cl	151°C	62%
4.	II_d		$C_{29}H_{23}O_2N_2S$ I	108°C	63%
5.	II_e		$C_{31}H_{25}ON_2S$ I	140°C	58%
6.	II_f		$C_{27}H_{21}O_2N_2S$ I	128°C	60%

RESULTS AND DISCUSSION

Compound $I_{(a)}$ – $I_{(f)}$and $II_{(a)}$ – $II_{(f)}$ were synthesized through the route as shown in general reactions R and R' as shown in table no. 1 & 2. Similarly, physical data as shown in table no. 1 and 2. The synthesized compounds 1,(I_a), (I_e) and II($_b$) were confirmed on the basis of IR, NMR spectral analysis.

Characterization data of compound
2-hydroxy-3-iodo-5-metyl acetophenone (1)
IR (KBr) ν max cm $^{-1}$
3200 cm^{-1} (s) – phenolic OH , 2919 cm^{-1} (s) – Aromatic C-H stretching , 1635 cm^{-1} C=O stretching , 1082 cm^{-1} (S) Ar-CH_3 - stretching , 1020 cm^{-1} (S) CH_3 stretching , 642 cm^{-1} C-I stretching .

H1 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).

2-hydroxy-3-iodo-5-methyl –phenyl chalcone. (I_a)
IR (KBr) ν max cm -^{1}
3412 cm^{-1} (br) – phenolic OH, 2917 cm^{-1} (S) AR-C-H- Stretching, 1746 cm^{-1} (S) C=O of O=C-CH=CH Stretching, 1358 cm^{-1} (S) C-O stretching in Phenol, 1264-1230 cm^{-1} (S) Ar-O stretching in ether, 563-548 cm^{-1} (S) C-I stretching.

H1 NMR: [δ CDCl3]
2.3-2.5 δ (S , 3H ,Ar- CH_3), 7.4 δ (S , 2H ,HC=CH), 7.5-7.9(m , 7H , Ar-H), 13.5 δ (br , 1H ,Ar-OH),

2-hydroxy-3-iodo-5-methyl –phenyl-4-phenyl ethenyl chalcone.(I_e)
IR (KBr) ν max cm -^{1}
3400 cm^{-1} (br) – phenolic OH, 2914 cm^{-1} (S) AR-C-H- Stretching, 1631 cm^{-1} (S) O=C-CH=C, 1353 cm^{-1}(S) C-O stretching in Phenol, 1230 cm^{-1}(S) Ar-O stretching in ether, 690.26 cm^{-1}(S) C-I stretching.

H1 NMR: [δ CDCl3]
2.1-2.3 δ (S , 3H ,Ar- CH_3), 2.8-3 δ (S , 1H ,O=C-CH), 5.2-5.3 δ (d , 2H ,HC=CH), 6.7-7.8 δ (m , 9H ,Ar-HC=CH &) (2H) & Ar-H (7H), 13.5-13.6 δ (br , 1H ,Ar-OH),

-4- (2'- hydroxy -3-iodo-5-methyl phenyl) -6- (-4- phenyl) - 2, 3-diphenyl- imino- 6H- 1, 3-thiazine. (II_a)
IR (KBr) ν max cm -^{1}
3460 cm^{-1} (br) – phenolic OH, 3206 cm^{-1} (S) C=N- streaching, 3033-3010 cm^{-1} (S) Ar-CH streaching ,Ar-CH3 streaching, 1449 cm^{-1} (S) C=N streaching, C=C streaching vibration in aryl group., 1341 cm^{-1} (S) C-N streaching, 818 cm^{-1} (S) C-I stretching

H1 NMR: [δ $CDCl_3$]
2.1 δ (S , 3H ,Ar- CH_3), 2.8-3.1 δ (d , 1H ,CH_A), 3.8 δ (d , 1H ,CH_B), 6.5-8.00 δ (m , 17H ,Ar-H), 8-8.1 δ (br , 1H ,Ar-OH),

CONCLUSION

Present study describes the synthesis of Chalcones and synthesis of 4,6 – diaryl-2-imino-2,3-diphenyl-6H-1,3-thiazines. Compounds were characterized by I.R.& N.M.R.

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REFERENCES

[1] M.Koketsu, K.Takanaka, Y.Takenaka, C.D.Kwong, and H.Ishihara, *Eur.J. Pharm.Sci*., **2002**, 15, , pp. 307-310.
[2] M.Koketsu, M.Okumura and H.Ishihara, *Heteroatom. Chem*, 2002, 13, pp. 377-379
[3] Nicolas Leftemme[a], Patrick Dallemagne[a], Sylvain Rault[a], *J. Tetrahydron Letters*, (9 Feb., **2004**), vol. 45, Issue 7, pages 1503-1505.
[4] X.F.Lin ., ., *Acta crystallographica section E*, (jully **2005**), vol. 61, part 7, , pp. o2207-o2208.
[5] Stefania De Montis, Claudia Fattuoni*, Enzo Cadoni, Maria G. Cabiddu, Michele Usai, Salvatore Cabiddu, *J. of Heterocyclic Chem*., **2008**, vol. 45, page no. 1445-1449.
[6] Fisyuk, A. S.', Peretokin, N. V.', Unkovsky, B. V.', *J. of chemistry of Heterocyclic compounds*, (June, **2003**), vol. 39, no. 6 pages 802-828 (7).
[7] V. N. Yuskovets', A. V. Moskvin' and B. A. Ivin', *Russian Journal of General Chemistry*, February **2004**, vol. 74, no. 2, , pages 312-313.
[8] M.Koketsu , M.Ebihara and H. Ishihara., *Acta crystallographica section E*, (may **2006**), vol. 62, part 5, pp. o1666-o1668.
[9] Norbert G. De Kimpe and Maria Teresa Rocchetti., *J. Agric. Food Chem*., **1998**, 46, (6), pp. 2278-2281.
[10] M. Koketsu, M. Ebihara and H. Ishihara, *J. of Acta Crystallographica Section E*, (April, **2006**), vol. 62, Part 4 pages 01218-01220

[11] Motomu Muraoka, Alsushi Yamada, Tatsuo Yamamoto, *J. of Heterocyclic Chem.*, Published Online 3 April, **2009**, vol. 21, Issue 4, , pages 953-955.
[12] Motomu Muraoka , Masataka Yokoyama , Kiyoko Yamomoto and Tatsuo Ttakeshima., *Bulletin of chemical society of japan* , (**1970**), vol. 43, no. 7 , pp. 2134 -2137.
[13] N.Ingarsal, P.Amutha, S.Nagrajan, *J.of Sulfur chemistry*, October. **2006**, vol.27,Issue 5, , pp. 455-459.
[14] Dipti R. Patil, Sonali M. Solunkhe, Mayur M.Aitawale, Madhukar B. Deshmukh , Govind B. Kolekar, and Prashant V. Anbule., *J. der pharma chemica*, **2011**,vol. 3, issue. 1, pp. 207-214.
[15] A.Nagaraj and C. Sanjeeva Reddy, *J. Iran. Chem. Soc.*, June, **2008**, vol.5, no. 12, pages 262-267.
[16] Ujawala Sawarkar, Meghsham Narule and Mahendra Choudhari., *J. der pharma chemica*,**2012** vol. 4, issue. 3, pp. 967-971.
[17] M.S.A.EL-Gaby, N.M.Saleh, J.A.Micky, Y.A.Ammar, H.S.A.Mohamed., *J of Phosphours, sulfur and silicon and related element*, june **2006**,vol. 181, issue 7,pp. 1655-1663.
[18] Ibadur R.Sddique and Pravin K. Singh., *Indian J. of chemistry*, march. **2007**, vol.46 B, pp. 499-504.
[19] Naresh Kumar and Ashok K. Yadav., *Indian J. of chemistry*, may **2008**, vol. 47 B, pp. 748-752.