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SYNTHESIS OF IODO-FLAVANONES AND CHROMANONES

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ABSTRACT

The mixture of 1-(2-hydroxy-3-iodo-5-methyl phenyl)-3-phenyl-1, 3-propanedione and six different aromatic aldehydes were refluxed in ethanol containing few drops of piperidine for 30 min. Thus synthesized flavanone **IIa-IIf**. The synthesized compounds were characterized by I.R. and N.M.R. spectral analysis.

Key words: Synthesis of iodo diketone, Flavanones, Chromanones.

INTRODUCTION

The treatment of 2'-hydroxychalcones with Co (salpr) in methanol under oxygen[1], $K_3Fe(CN)_6$ using phase transfer catalysis[2], and photochemical irradiation[3] gives flavanones, but the yields are mostly low to moderate. 2'-Hydroxychalcones are also converted to flavanones by the treatment with acidic reagents such as H_2SO_4 in methanol[4].

Choudary et al.[5] have synthesized flavanone using nanocrystalline MgO. Biddel et al.[6] have studied catalytic enantioselective synthesis of flavanone and chromanones. Nibbs and Scheidt[7] have studied asymmetric method for the synthesis of flavanones, chromanones and azaflavanones. Sagrera and Seoane[8] have synthesized microwave accelerated solvent-free synthesis of flavanones. Boumendjel et al.[9] have studied efficient synthesis of flavanone glucuronides. Lee et al.[10] have reported a novel synthesis of flavanone from 2-hydroxybenzoic acids. Alternatively flavanones are prepared by the cyclization of 3-bromo-1-phenylprop-2-ynyl aryl ethers in the presence of Hg $(OCOCF_3)_2$ after $NaBH_4$ workup[11] or the dehydration/cyclization of 3-hydroxy-1-*o*-hydroxyphenyl-3-phenylpropan-1-ones derived from isoxazoles[12].

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EXPERIMENTAL

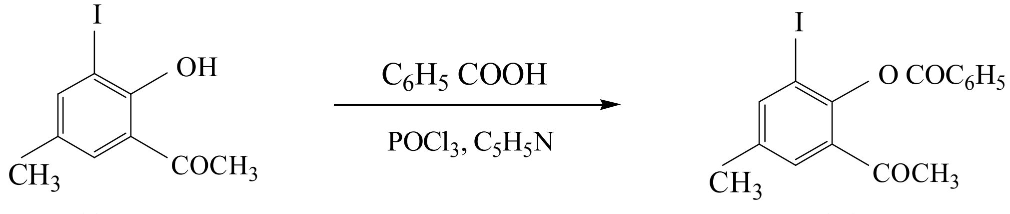
Melting points of all synthesized compounds were determined in open capillary tube and are uncorrected. The purity of compounds was checked by TLC using silica G.I.R. Spectra were recorded on Perkin-Climer-841 spectrometer (cm^{-1}) in KBr disc and NMR (Brucker Avance II 400 NMR) using $CDCl_3$ as solvent.

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

p-Cresol was converted to p-cresyl acetate by known method and then by Fries migration 2-hydroxy-5-methyl acetophenone was prepared, which on iodination gives 2-hydroxy-3-iodo-5-methyl acetophenone **(I)**.

Synthesis of 2-benzoyl-oxy-3-iodo-5-methyl-acetophenone (II)

2-Hydroxy-3-iodo-5-methyl acetophenone **(**15 g) and benzoic acid (12.2 g) were dissolved in dry pyridine 60 mL. Phosphorous oxychloride (9 mL) was added dropwise with constant stirring and external cooling during the addition of $POCl_3$ (temp. 50°C). It was kept steady for about 4 to 5 hours at room temp. and then acidified with ice-cold HCl (1 : 1). The product was filtered, washed with water and then with $NaHCO_3$ 10% to remove unreacted aromatic acid. Further, it was washed with dil. NaOH 1% followed by water to remove unreacted phenolic ketone. It was dried and crystallized from ethanol to give compound **(II)** M.P. 96°C. Yield 81% .



(I) **(II)**

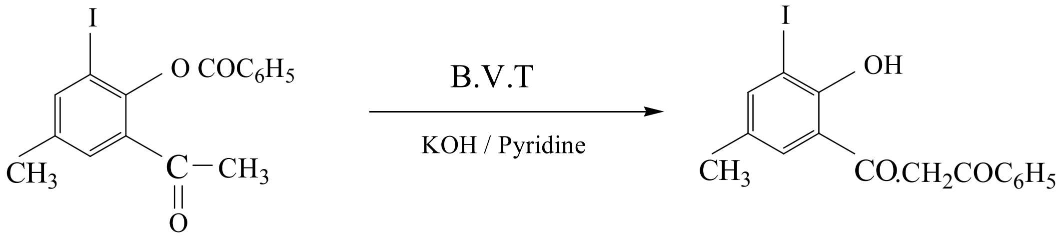
Scheme 1

Synthesis of diketone (III)

1-(2-Hydroxy-3-iodo-5-methyl phenyl)-3-phenyl-1, 3-propanedione (III)

Benzoyl-oxy-3-iodo-5-metyl acetophenone (0.15 mol, 13.78 g) was placed in anhydrous pyridine (60 mL) at 50°C. Pulverized KOH (14 g) was added in small installment with constant stirring. Vigorous reaction takes place and on mixing, it begans to thicken. It was warmed again when yellowish red mass was obtained. It was allowed to stand for about 5 to 6 hours. Then decomposed by ice-cold 1 : 1 HCl, filtered, washed with 10% $NaHCO_3$

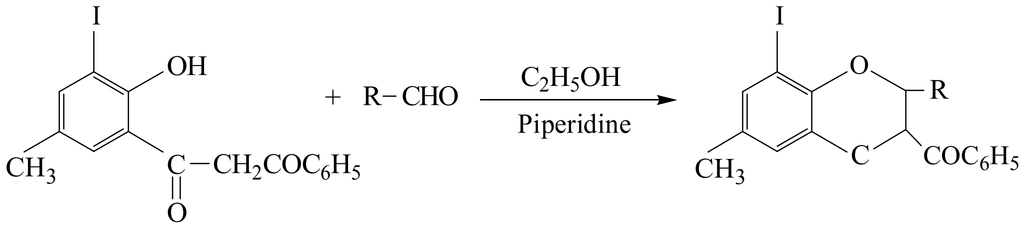
solution successively and product was crystallized from ethanol to get lemon yellow shining crystals of compound **(III)**. M.P. 120-130°C, yield 82 %.



(II) **(III)**

Synthesis of flavanones and chromanones

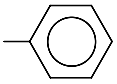
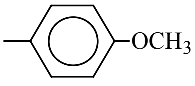
A mixture of 1-(2-hydroxyl-3-iodo-5-metyl)-3-phenyl-1,3-propanedione **(III)** (0.02 M) and six different aromatic aldehydes (0.02 M) were refluxed in 30 mL ethanol containing piperidine (0.5 mL) and refluxed for 30 min. Reaction mixture was cooled for half an hour, when slight whitish product was obtained, which was filtered, washed and crystallized from ethanol-AcOH mix to gets shining needles shapes crystals of compound **(IVa-IVf)**.



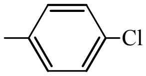
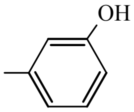
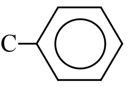
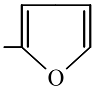
(III) **(IVa – IVf)**

The groups R are shown in Table 1.

Table 1.

Compound	**R**	**Mol. Formula**	**M.P. (°C)**	**Yield (%)**
IVa		$C_{23}H_{17}O_3I$	117	76
IVb		$C_{24}H_{19}O_4I$	76	68

Cont…

Compound	**R**	**Mol. Formula**	**M.P. (°C)**	**Yield (%)**
IVc		$C_{23}H_{16}O_3ICl$	122	70
IVd		$C_{23}H_{17}O_4I$	110	66
IVe	-HC=HC-	$C_{25}H_{19}O_3I$	98	63
IVf		$C_{20}H_{15}O_4I$	86	65

Characterization data of compound (I)

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

R (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.

^{1}H NMR: [$CDCl_3$] 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-Benzoyl-oxy-3-iodo-5-methyl acetophenone (II)

IR (KBr) ν_{max} cm^{-1}: 3046 cm^{-1} (s) – Aromatic C-H stretching in Ar-H, 2919 cm^{-1} (s) – C-H stretching in CH_3, 1686 cm^{-1} C=O stretching, 1212.5 cm^{-1} (s) O-C=O stretching, 1562.09 cm^{-1} (s) C=C ring **s**tretching, 862.11 cm^{-1} (s) =C-H out of plane aromatic ring, 792.06 cm^{-1} (s) C-I stretching.

^{1}H NMR: [$CDCl_3$] 2.25 δ (S, 3H, Ar- CH_3), 2.6 δ (S, 3H, Ar-CO- CH_3), 7.5-8.25 δ (m, 7H, Ar-H), 13 δ (S, 1H, Ar-OH).

1-(2-Hydroxy-3-iodo-5-methyl phenyl)-3-phenyl-1,3-propanedione (III)

IR (KBr) ν_{max} cm^{-1}: 3420 cm^{-1} (br) Ar-OH stretching, 3045 cm^{-1} (s) Ar-H-stretching, 2919 cm^{-1} (s) Ar-CH_3 stretching, 1635 cm^{-1} (s) C=O stretching, 1598 cm^{-1} (s) C=C stretching, 695 cm^{-1} (s) C-I stretching.

^{1}H NMR: [$CDCl_3$] 2.1-2.3 δ (S, 3H, Ar- CH_3), 7.5-7.85 δ (m, 7H, Ar-H), 8.25 δ (d, 2H, CH_2), 12.8 δ (S, 1H, Ar-OH)

3-Benzoyl-4'-methoxy phenyl-6-methyl- 8-iodo flavanone (IVb)

IR (KBr) ν_{max} cm^{-1}: 3350.73 cm^{-1} (br) Ar-OH stretching, 3356.38 cm^{-1} (s) Ar-CH-stretching, 2914.56 cm^{-1} (s) Ar-CH_3 stretching, 1692.35 cm^{-1} (s) C=O stretching of aroyl group, 1349.47 cm^{-1} (s) pyrone, 1253.64 cm^{-1} (s) Ar-O,1464-1439 cm^{-1} (s) C=C stretching vibration in aryl group, 696.15 cm^{-1} (s) C-I stretching.

^{1}H NMR: [$CDCl_3$] 2.2-2.40 δ (S, 3H, Ar- CH_3), 3.8 δ (S, 3H, Ar-OCH_3), 3.00 δ (S, 1H, CH_A), 5.5 δ (S, 1H, CH_B), 6.8-7.9 δ (m, 11H, Ar-H), 12.9 δ (S, 1H, Ar-OH).

RESULTS AND DISCUSSION

Compound No. **I, II, (IVa)-(IVf)** were synthesized through the route as shown in general reactions and R as shown in Table. Similarly, physical data are shown in Table 1. The synthesized compounds No. **I, II** and **IVb** were confirmed on the basis of IR and NMR spectral analysis.

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