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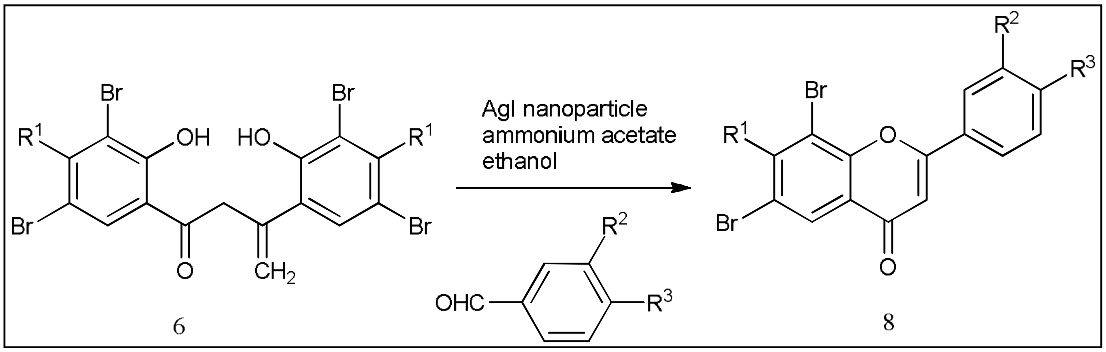
Silver Iodide Nanoparticles Catalysed Synthesis of 6, 8-dibromoflavones

Shanmugasamy Ponmuthumariammal[1], Arumugasamy Vanangamudi[2]
[1]*Chemistry Department, Ayya Nadar Janaki Ammal College/Madurai Kamaraj University, India*
[2]*Chemistry Department, Ayya Nadar Janaki Ammal College/Madurai Kamaraj University, India*

Graphical Abstract:



R^1 = OMe / OEt, $R^2 = NO_2$, R^3 = Cl, Br, $NHCOCH_3$, NO_2

***Abstract:** Dibromo flavones have been synthesized by using silver iodide nanoparticles catalyzed Mannich base condensation of arylaldehyde with 1,3-bis(3,5-dibromo-4--alkoxy-2-hydroxyphenyl)-but-3-en-1-one in presence of ammonium acetate. A comparative study on the synthesis of 6,8-dibromoflavones using with and without silver iodide nanoparticles catalys have been carried out. The reaction carried out with silver iodide nanoparticles resulted in the excellent yield of 6,8-dibromoflavones in short reaction times.*

***Keywords:** synthesis, AgI nanoparticles, 6,8-dibromoflavones*

I. INTRODUCTION

Nanotechnology is an important field of modern research dealing with design, synthesis, and manipulation of particles structure ranging from approximately 1-100 nm. Silver nanoparticles are of interest because of the unique properties (*e.g.*, size and shape depending optical, electrical, and magnetic properties) which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products, and electronic components. Several physical and chemical methods have been used for synthesizing and stabilizing silver nanoparticles.[1,2] The most popular chemical approaches, including chemical reduction using a variety of organic and inorganic reducing agents, electrochemical techniques, physicochemical reduction, and radiolysis are widely used for the synthesis of silver nanoparticles. Recently, nanoparticle synthesis is among the most interesting scientific areas of inquiry, and there is growing attention to produce nanoparticles using environmentally friendly methods. Last decade has witnessed significant growth in the field of nanoscience and nanotechnology. Several reports showed an amazing level of the performance of nanoparticles as catalyst in terms of selectivity, reactivity, and improved yields of products.[3] In addition; the high surface-to-volume ratio of nanoparticles provides a larger number of active sites per unit area in comparison with its heterogeneous counter parts. Among various metal nanostructures, silver nanoparticles have received great attention because of their unusual properties and potential applications in diverse fields.[4] In comparison with traditional catalysts, silver nanoparticles, in particular, being available, require only mild reaction conditions to produce high yields of products in short reaction times and can also be recycled.[5] Recently, silver nanoparticles were used as an active catalysts in many organic reactions such as, three-component coupling of aldehyde-amine-alkyne,[6] carbon–carbon coupling reaction,[7] dehydrogenation reaction,[8] oxidation reaction,[9] Diels–Alder cycloadditions of $2'$-hydroxychalcones[10] and synthesis of β-enaminones.[11] In view of the above facts, In the present work, the silver iodide nanoparticles catalysed synthesis 6,8-dibromo-7-methoxy/ethoxyflavones have been carried out.

II. EXPERIMENTAL PROCEDURE

All solvents were purchased from commercial sources and used without further purification. The melting points were measured in open capillary tubes and are uncorrected. The IR spectra were recorded on an 8400S SHIMADZU spectrophotometer and the UV-spectra on a SHIMADZU UV-1700 UV-vis spectrophotometer. Nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300-MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million (δ), coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quatret), sept (septet), m (multiplet). Thin layer chromatography (TLC) was carried out on Merck silica gel.

A. Preparation of silver iodide nanoparticles

A solution of 0.415 g KI (25 x 10^{-4} mol) in 25 ml distilled water was added drop-wise to $AgNO_3$ solution (0.425 g, 25 x 10^{-4} mol in 25 ml distilled water) under ultrasound power in the presence of 0.2 g sodium dodecyl sulphate (SDS) as surfactant. The yellow precipitate was separated by centrifugation and washed with distillated water and ethanol to remove impurities for several times and then dried.[12]

B. Synthesis of 2,4-dihydroxyacetophenone

Fused zinc chloride (0.05 M) was added to glacial acetic acid (15 ml) in a beaker kept over a burner. Resorcinol (0.1 M) was added when the temperature reached 110° C. The temperature was slowly raised to 140° C and maintained at the temperature for 15 minutes. The reaction mixture was cooled and the syrupy liquid is treated with HCl (1:1, 80 ml). The crystalline mass is filtered and recrystallised from hot water.

M.P: 143-144 °C (lit.[13] m.p. 142-144 °C) Yield : 95 %

C. Synthesis of 1-(2-hydroxy-4-methoxy/ethoxyphenyl) ethanone

2,4-Dihydroxyacetophenone (0.02 M) was dissolved in dry acetone and refluxed for 3 hours with dimethyl/ethyl sulphate (0.02 M) in the presence of anhydrous potassium carbonate (10 g). After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the potassium salts were washed with several portions of acetone. The combined filtrate was distilled to remove the solvent and the residue was treated with ice-cold water and neutralized with concentrated hydrochloric acid, when 1-(2-hydroxy-4-methoxy/ethoxyphenyl) ethanone separated as a solid. It was crystallized from ethanol as white crystals. It gave deep red colour with neutral ferric chloride.

M.P: 50-51 °C (lit.[14] m.p. 52-53 °C) Yield : 90 %
M.P: 55-56 °C (lit.[15] m.p. 54-55 °C) Yield : 90 %

D. Synthesis of 1-(5-bromo-2-hydroxy-4-methoxyphenyl)ethanone

1-(2-Hydroxy-4-methoxyphenyl)ethanone (0.01 M) was dissolved in 10 ml of glacial acetic acid in a 100 mL conical flask. Bromine (0.75 ml, 0.005 M) was added to this solution from a dropping funnel, shaking the mixture vigorously. After the completion of the reaction (monitored by TLC), the reaction mixture was treated with ice-cold water, when 1-(5-bromo-4-methoxy-2-hydroxyphenyl)ethanone separated as a solid. It was crystallized from ethanol as colourless needles.

M.P: 168-170 °C (lit.[15] m.p. 166-170 °C) Yield : 70 %

E. Synthesis of 1-(3,5-dibromo-4-ethoxy-2-hydroxyphenyl)ethanone

1-(2-Hydroxy-4-ethoxyphenyl)ethanone (0.01 M) was dissolved in 10 ml of glacial acetic acid in a 100 mL conical flask. Bromine (0.75 ml, 0.005 M) was added to this solution from a dropping funnel, shaking the mixture vigorously. After the completion of the reaction (monitored by TLC), the reaction mixture was treated with ice-cold water, when 1-(3,5-dibromo-4-ethoxy-2-hydroxyphenyl)ethanone separated as a solid. It was crystallized from ethanol as colourless needles.

M.P: 157-159 °C (lit.[15] m.p. 158-160 °CYield : 75 %

F. Synthesis of 1,3-bis(3,5-dibromo-2-hydroxy-4-methoxy/ethoxyphenyl)but-3-en-1-one

1-(5-Bromo-4-methoxy-2-hydroxyphenyl)ethanone/ 1-(3,5-dibromo-4-ethoxy-2-hydroxyphenyl)ethanone (0.01 M) was dissolved in 10 ml of chloroform and 5 ml of glacial acetic acid in a 100 mL conical flask. About 0.75ml (0.005 M) of bromine was added to this solution from a dropping funnel, shaking the mixture vigorously during the period of 30 minutes. After the completion of the

reaction (monitored by TLC), the reaction mixture was treated with ice-cold water. The viscous mass obtained was extracted with diethyl ether (2 × 25 ml), washed with water and dried over anhydrous sodium sulphate (2 g). Evaporation of ether gave 1,3-bis(3,5-dibromo-4-methoxy/ethoxy-2-hydroxyphenyl)but-3-en-1-one as a semi-solid. It was crystallized from ethanol as pale yellow coloured crystals.
M.P: 92-94 ºC (lit.[15] m.p. 91-93 ºC Yield : 75 %
M.P: 89-91 ºC (lit.[15] m.p. 88-90 ºC) Yield : 70 %

G. General method for the synthesis of 6,8-dibromo-7-methoxy/ethoxy flavones (8a-f)

An ethanolic solution of 1,3-bis(3,5-dibromo-4-methoxy/ethoxy-2-hydroxyphenyl)but-3-en-1-one (0.005 M), arylaldehydes (0.005 M), ammonium acetate (0.01 M) and 0.2 g of silver iodide nanoparticle were taken in a 50 mL beaker. The mixture was heated in a water bath for 5 minutes. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered. The silver iodide nanoparticle was washed with several portion of chloroform and the combined filtrates were evaporated. Then the reaction mixture was treated with ice-cold water and neutralized with concentrated hydrochloric acid. The residue was crystallised from ethanol as colourless crystals. It was negative towards neutral ferric chloride solution.

H. Synthesis of 6,8-dibromo-2-(4-chlorophenyl)-7-methoxy-4h-chromen-4-one (8a)

Colourless crystals, M.p. 144 ºC (lit.[15] m.p. 141-145 ºC), UV (EtOH) λ_{max} (nm): 340, 271, IR (KBr) (cm^{-1}): 824 (C-Br); 890 (C-Cl); 1173 (C-O); 1594 (C=C); 1652 (C=O); 2856 (aliphatic CH); 3073 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 4.02 (3H, s, OCH_3); 6.88 (1H, s, H-3); 7.45 (2H, d, *J* = 9 Hz, H-2', 6'); 7.86 (2H, d, *J* = 9 Hz, H-3', 5'); 7.96 (1H, s, H-5).

I. Synthesis of 6,8-dibromo-2-(4-bromophenyl)-7-methoxy-4h-chromen-4-one (8b)

Colourless crystals, M.p. 199 ºC (lit.[15] m.p. 198-200 ºC), UV (EtOH) λ_{max} (nm): 341, 292, IR (KBr) (cm^{-1}): 811 (C-Br); 1173 (C-O); 1596 (C=C); 1654 (C=O); 2943 (aliphatic CH); 3071 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 4.02 (3H, s, OCH_3); 6.85 (1H, s, H-3); 7.61 (2H, d, *J* = 6 Hz, H-2', 6'); 7.78 (2H, d, *J* = 9 Hz, H-3', 5'); 7.95 (1H, s, H-5).

J. Synthesis of n-(4-(6,8-dibromo-7-methoxy-4-oxo-4h-chromen-2-yl)phenyl)acetamide (8c)

Colourless crystals, M.p. 253 ºC (lit.[15] m.p. 252-254 ºC), UV (EtOH) λ_{max} (nm): 351, 271, IR (KBr) (cm^{-1}): 832 (C-Br); 1169 (C-O); 1596 (C=C); 1668 (C=O); 2943 (aliphatic CH); 3182 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 2.24 (3H, s, $COCH_3$); 4.02 (3H, s, OCH_3); 6.92 (1H, s, H-3); 7.35 (1H, s, NH); 7.65 (2H, d, *J* = 9 Hz, H-2', 6'); 7.93 (2H, d, *J* = 9 Hz, H-3', 5'); 7.97 (1H, s, H-5).

K. Synthesis of 6,8-dibromo-7-methoxy-2-(3-nitrophenyl)-4h-chromen-4-one (8d)

Colourless crystals, M.p. 223 ºC, UV (EtOH) λ_{max} (nm): 336, 262, IR (KBr) (cm^{-1}): 820 (C-Br); 1174 (C-O); 1530 (N-O); 1594 (C=C); 1655 (C=O); 2870 (aliphatic CH); 3065 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 4.04 (3H, s, OCH_3); 6.95 (1H, s, H-3); 7.68 (1H, t, *J* = 9 Hz, H-5'); 7.99 (1H, s, H-5); 8.18 (1H, d, *J* = 6 Hz, H-6'); 8.29 (1H, d, *J* = 6 Hz, H-4'); 8.92 (1H, s, H-2').

L. Synthesis of 6,8-dibromo-7-methoxy-2-(4-nitrophenyl)-4h-chromen-4-one (8e)

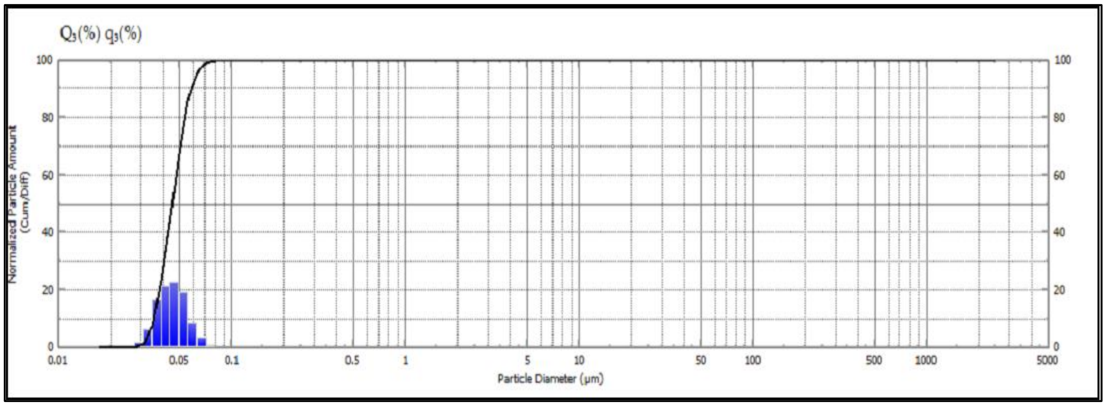
Colourless crystals, M.p. 202 ºC (lit.[15] m.p. 200-203 ºC), UV (EtOH) λ_{max} (nm): 338, 265, IR (KBr) (cm^{-1}): 848 (C-Br); 1174 (C-O); 1513 (N-O); 1598 (C=C); 1650 (C=O); 2855 (aliphatic CH); 3071 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 4.04 (3H, s, OCH_3); 6.92 (1H, s, H-3); 7.98 (1H, s, H-5); 8.08 (2H, d, *J* = 9 Hz, H-2', 6'); 8.33 (2H, d, *J* = 9 Hz, H-3', 5').

M. Synthesis of 6,8-dibromo-2-(4-chlorophenyl)-7-ethoxy-4h-chromen-4-one (8f)

Colourless crystals, M.p. 176 ºC (lit.[15] m.p. 176-177 ºC), UV (EtOH) λ_{max} (nm): 341, 270, IR (KBr) (cm^{-1}): 820 (C-Br); 895 (C-Cl); 1172 (C-O); 1594 (C=C); 1650 (C=O); 2980 (aliphatic CH); 3071 (aromatic CH), ^1H NMR (300 MHz, $CDCl_3$): δ 1.56 (3H, t, *J* = 9 Hz, CH_3); 4.21 (2H, q, *J* = 6 Hz, OCH_2); 6.86 (1H, s, H-3); 7.44 (2H, d, *J* = 9 Hz, H-2', 6'); 7.85 (2H, d, *J* = 9 Hz, H-3', 5'); 7.94 (1H, s, H-5).

III. RESULTS AND DISCUSSION

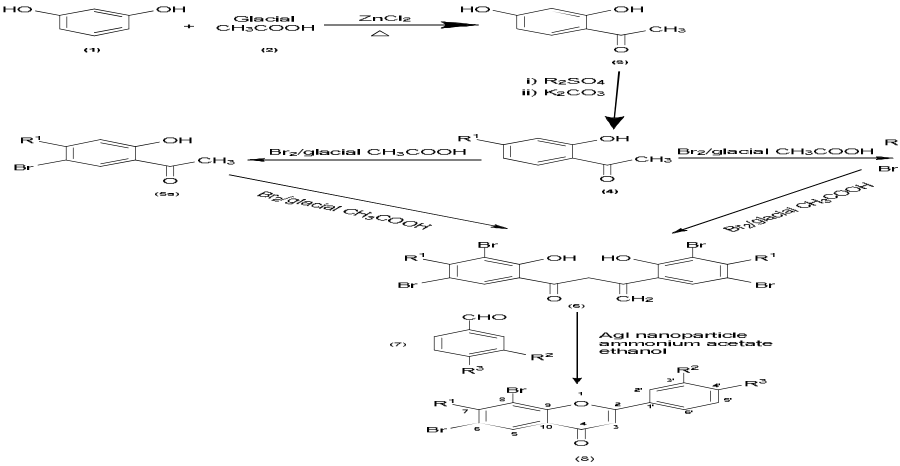
The catalyst silver iodide nanoparticle required for the synthesis of 6,8-dibromo-7-methoxy/ethoxy flavones (8a-f) was prepared by the addition of potassium iodide solution to the silver nitrate solution in drop-wise under ultrasound power in the presence of sodium dodecyl sulphate (SDS) as surfactant. The obtained yellow precipitate was separated by centrifugation and washed with distilled water and ethanol to remove impurities for several time and then dried.[12] The size of the silver iodide nanoparticle was analysed by particle size analyser and found to be 45 nm.



Particle size analyzer of the silver iodide nanoparticles

A. Synthesis of 6,8-dibromo-7-methoxy/ethoxyflavones (8a-f)

The title compounds 6,8-dibromo-7-methoxy/ethoxyflavones (8a-f) were prepared by heating an equimolar amounts of the corresponding 1,3-bis(3,5-dibromo-4-methoxy/ethoxy-2-hydroxyphenyl)but-3-en-1-one (6) and arylaldehyde in the presence of AgI nanoparticle in presence of ammonium acetate (Scheme-I). All the compounds were negative towards neutral ferric chloride. The amount of AgI nanoparticles required for the synthesis of title compounds (8a-f) was optimized by carried out the synthesis by using different amount of AgI nanoparticle (100 mg, 200 mg , 300 mg, 400 mg, 500 mg). The better yield was obtained when the reaction was carried out with 200 mg of AgI nanoparticles in short duration. There was no more significant effect on the product yield or reaction time beyond 200 mg of the AgI nanoparticles. The generality of this reaction was examined by using electron withdrawing substituents on the aldehydes under the same reaction conditions and observed that the yields are good irrespective of the substituents present. The product yield and time have been compared for the reaction carried out with and without silver iodide nanoparticles catalyst (Table I). At the end of the reaction, the catalyst was recycled and reused.



	R1
5a	OMe
5b	OEt

	8a	8b	8c	8d	8e	8f
R1	OMe	OMe	OMe	OMe	OMe	OEt

R^2	H	H	H	NO_2	H	H
R^3	Cl	Br	$NHCOCH_3$	H	NO_2	Cl

Scheme I: Synthesis of 6,8-dibromo-7-methoxy/ethoxyflavones

Table I: Comparison between the synthesis of 6,8-dibromo-7-methoxy/ethoxyflavones with and without AgI nanoparticles catalyst

Compound	Reaction period without AgI np's (min)	Yield (%)	Reaction period with AgI np's (min)	Yield (%)
8a	15	80	5	92
8b	15	80	5	93
8c	15	80	5	90
8d	15	79	5	95
8e	15	75	5	85
8f	15	75	5	85

The results showed that better yield have been achieved when the reaction was carried with silver iodide nanoparticle in shorter reaction time.

B. Characterisation of compounds (8a-f)

The synthesized compound was characterized by UV-vis., FTIR and ^1H NMR spectra. The UV-vis. spectra of the compounds (8a-f) in ethanol showed two maxima one around at 262-292 nm and another at 336-351 nm. The infrared spectra of the compounds (8a-f) showed carbonyl absorption in the region 1650-1668 cm^{-1}. In the ^1H NMR spectra of the compounds (8a-f) showed the flavones, apart from the expected aromatic protons in the region 7.35-8.92 δ, two singlets each integrating to one proton observed in the region 7.94-7.99 δ and 6.85-6.95 δ were assigned to H-5 and H-3 protons respectively.

IV. CONCLUSIONS

In summary, we have developed a new method for the synthesis of 6,8-dibromoflavone and increase the yield and reduce time for the synthesis of 6,8-dibromo-7-methoxy/ethoxyflavones by using AgI nanoparticles as a catalyst. Moreover, this method has the major advantages of short reaction time, good yield, simple workup and green approach.

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