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Synthesis And Characterization Of Novel Series Of 3(2- Aryl Methylidene Hydrazinyl) - 2h-Chromene-2-One

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ABSTRACT

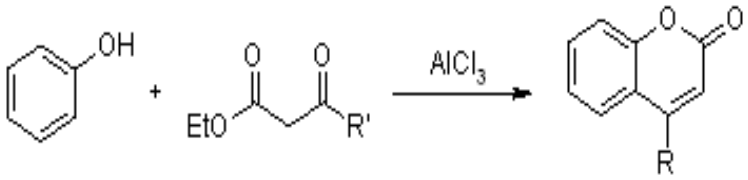
A novel series of 3(2-aryl methylidene hydrazinyl)-2H-Chromene-2-one (4f-ad) were synthesized. Condensation of salicylaldehyde(5a) with Dimethyl malonate(5b) in the presence of a base (piperidine) gave 2-oxo-2H-chromen-3yl-acetate (4f-ab) while (4f-ab) further react with hydrazine hydrate gave 3-hydrazinyl 2H-Chromene-2-one(4f-ac).Condensation of (4f-ac) with aromatic aldehyde gave 3(2-aryl methylidene hydrazinyl)-2H-Chromene-2-one(4f-ad).The structures of the newly synthesized compounds were confirmed by their spectra data of IR, ^{1}H-NMR.

Keywords: Coumarin, methylidene hydrazinyl, Pechmann condensation.

INTRODUCTION

Coumarin and its derivatives represent one of the most active classes of compound possessing a wide spectrum of biological activity [1–4]. Many of these compounds have proven to be active as antibacterial [5–7], antifungal [8], anti-inflammatory [9], anticoagulant [10], anti-HIV [11] and antitumor agents [12].Coumarins are widely used as additives in food, perfumes, cosmetics [13], pharmaceuticals and optical brighteners [14] and would dispersed fluorescent and laser dyes [15]. Coumarins also have the super thermal stability and outstanding optical properties including extended spectral response, high quantum yields and superior photo stability. Optical applications of these compounds, such as laser dyes, nonlinear optical chromophores, fluorescent whiteners, fluorescent probes, polymer science, optical recording and solar energy collectors have been widely investigated [16–20].Classical routes to coumarins incorporate Pechmann, Knoevenagel, Perkin, Reformatsky, and Wittig-condensation reactions [21–24]. The two most important methods for the synthesis of Coumarin derivatives are due to Perkin and Pechmann [25-26].The naturally occurring coumarins have been obtained either (i) by the closure of the lactone ring with the necessary substituents in the benzene nucleus, or (ii) by the introduction of the substituents in the requisite coumarin. The action of the sodium salt of an aliphatic acid and its anhydride on an o-hydroxy- aldehyde acid with the intermediate formation of o-hydroxy-cinnamic acid **(Perkin method)** and the action of malic acid on phenol in the presence of sulphuric acid **(Pechmann's method)** have been very convenient method for the synthesis of coumarins. The o-hydroxy-cinnamic acids have been also prepared by other method and they easily lactonize to coumarins.

Coumarin Synthesis



The Pechmann Condensation allows the synthesis of coumarins by reaction of phenols with β-keto esters.

MATERIALS AND METHODS

Drugs and Chemicals: A typical synthetic strategy employed to obtain the title compound in excellent yield is depicted in scheme. In the present investigation,3(2-aryl methylidene hydrazinyl)-2H-Chromene were obtained from 2-oxo-2H-chromen-3yl-acetate and 3-hydrazinyl-2H-Chromen-2-one using ethanol as a solvent and in the scheme first using piperidine as a base. All reagents were of the highest purity commercially available.

Experimental: The reagents were all analytically pure. All solvents and liquid reagents were dried by standard methods in advance and distilled before use. All the reactant compounds were bought from the Sigma Aldrich ltd. Reaction are monitored by thin-layer chromatography (TLC) on silica gel 60 F^{254}aluminium sheet .The mobile phase was ethylacetate: methanol (9: 1) and detection was made using iodine chamber. The infrared (IR) spectra were recorded on a FTIR Shimadzu 8400 meter using potassium bromide pellets. 1H NMR spectra were recorded on a JEOL AL3OO FTNMR , CHEMISTRY DEPARTMENT Banaras Hindu University, Varanasi-221005 in $CDCl_3$ or DMSO-d6 with TMS as the internal reference The chemical shifts are expressed in part per million (ppm) downfield from the internal standard; the coupling constants are in Hz, and signals are quoted as*s*(singlet), *d*(doublet), *t* (triplet), *q* (quartet), or *m* (multiplet).Melting points were determined using open capillary tube in Toshniwal Melting point apparatus and are presented without any correction.

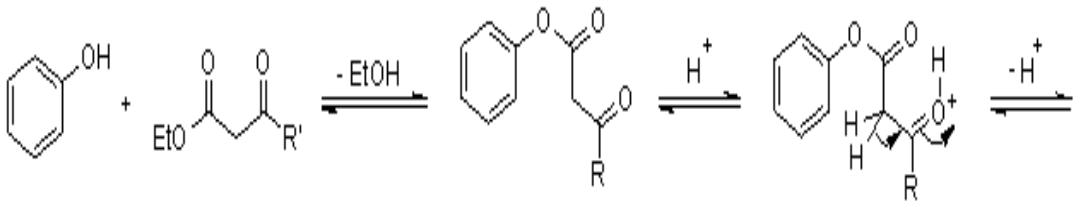
Synthesis

2-oxo-2H-chromen-3yl-acetate (4f-ab): In a 500-ml. round-bottomed flask equipped with a reflux condenser are placed 61 g. (0.50 mol) ofsalicylaldehyde,88 g. (0.55 mol) of ethyl malonate, and 200 ml. of absolute ethanol. To this mixture add 5 ml. of piperidine and 0.5 ml. of glacial acetic acid and the solution is heated under reflux for 3 h. The hot solution is transferred to a Erlenmeyer flask, the reaction flask is rinsed with 20 ml. of ethanol, and the ethanol rinse and 330 ml. of hot water are added to the solution. The product crystallizes readily as the solution cools; the mixture is stirred from time totime as crystallization proceeds and is finally stored overnight in a refrigerator. The crystalline product is collected by filtration and washed with a solution made from 80 ml. of 95% ethanol and 120 ml of water. The material is dried in the air. The product may be recrystallized by dissolving it in 200 ml. of hot ethanol (95%), filtering, and adding 315 ml. of hot water. The recrystallized product is washed on the filter with 200 ml. of aqueous ethanol, as before, and air-dried. The yield of white 3-carbethoxycoumarinis 70% ,m.p. 92–94°.

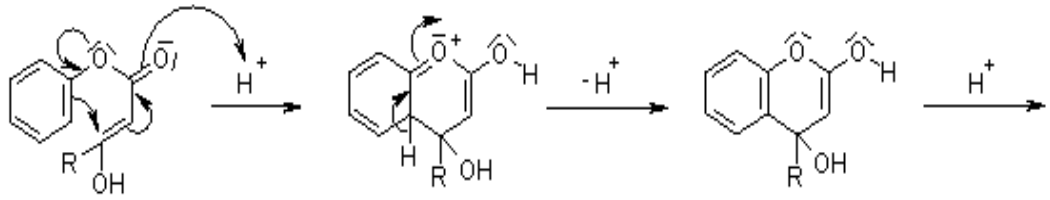
3-hydrazinyl-2H-Chromen-2-one(4f-ac): In a 20ml of hydrazine hydrate (98%) was refluxed 0.02mol of compound (4f-ab) for 2 h. The precipitate formed after cooling was filtered, washed with water, dried and recrystallized from ethanol.

3(2-aryl methylidene hydrazinyl)-2H-Chromene-2-one (4f-ad): For 2-6 h, 0.01mol of compound (4f-ac) and 0.011mol of appropriate aromatic aldehyde and25ml of ethanol(96%) were refluxed. The solid that separate was filtered and recrystallized from ethanol.

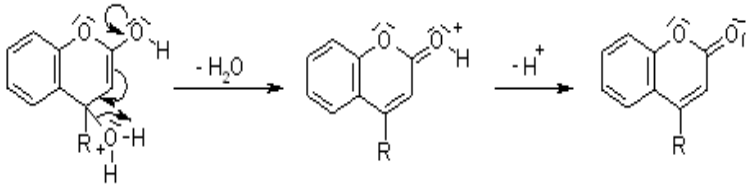
Mechanism of the Pechmann Condensation: The reaction is conducted with a strong Bronsted acid such as methane sulfonic acid or a Lewis acid such as $AlCl_3$. The acid catalyses trans-esterification as well as keto-enol tautomerisation



A Michael Addition leads to the formation of the coumarin skeleton. This addition is followed by re-aromatization:



Subsequent acid-induced elimination of water gives the product:

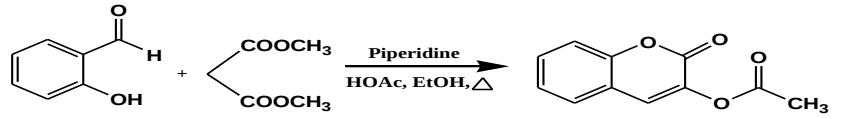


Characterization

Spectral discussion: IR spectra of the synthesized compounds were recorded on Shimadzu FT-IR 8400 model using KBr powder method. Various functional groups present were identified by characteristic frequency obtained for them.

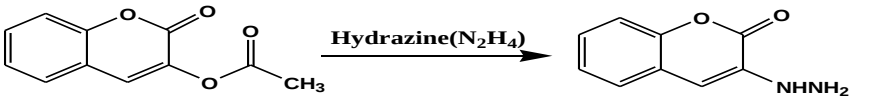
1H NMR spectra of the synthesized compounds were recorded on JEOL AL3OO NMR spectrometer by making a solution of samples in CDCl3/DMSO-*d*6 solvent using tetramethylsilane (TMS) as the internal standard unless otherwise mentioned. Number of protons identified from ^{1}H NMR spectra and their chemical shift (δ ppm) were in the agreement of the structure of the molecule. *J* values were calculated to identify o, m and p coupling. In some cases, aromatic protons were obtained as multiplet. Interpretation of representative spectrum is discussed here.

Reaction Scheme



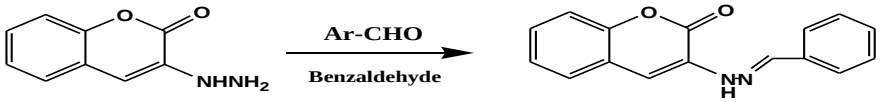
Salicylaldehyde **(5a)** Dimethyl malonate **(5b)** 2-oxo-2H-chromen-3yl-acetate **(4f-ab)**

Synthesis of 2-oxo-2H-chromen-3yl-acetate



2-oxo-2H-chromen-3yl-acetate **(4f-ab)** 3-hydrazinyl 2H-chromen-2-one **(4f-ac)**

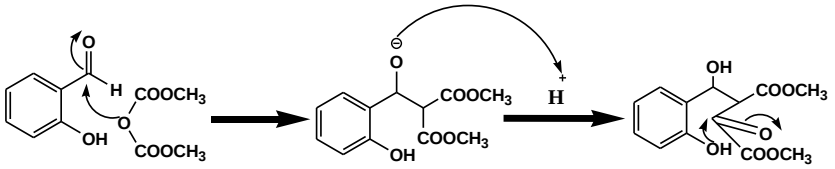
Synthesis of 3-hydrazinyl 2H-chromen-2-one.

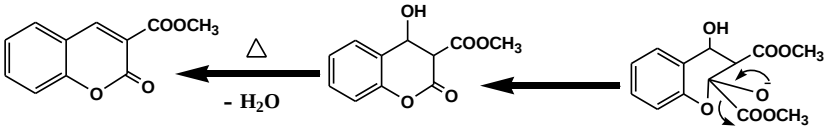


3-hydrazinyl 2H-chromen-2-one **(4f-ac)** 3(2-aryl methylidene hydrazinyl)-2H-chromen-2-one **(4f-ad)**

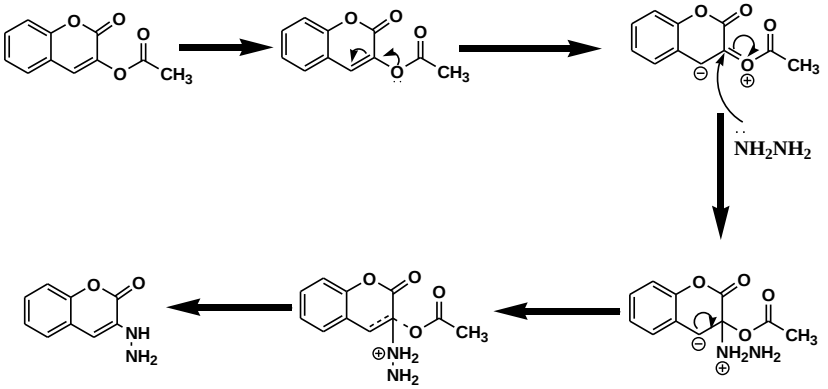
Synthesis of 3(2-aryl methylidene hydrazinyl)-2H-chromen-2-one.

MECHANISM OF SCHEME 1-

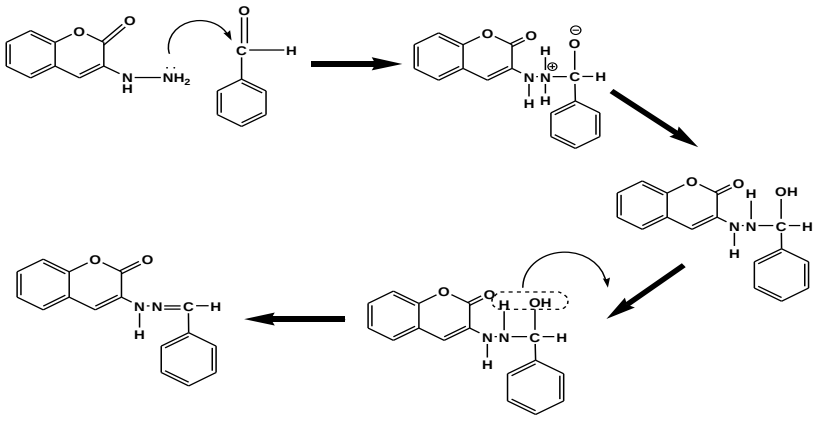




MECHANISM OF SCHEME 2



MECHANISM OF SCHEME 3-



Compound (4f-ab): Infrared spectrum (cm^{-1} ,KBr)–were obtain by reaction of salicylaldehyde with dimethyl malonate in the presence of a base. The spectrum of compound absorb at 1685 cm^{-1}, show the presence of –C=O Group of ester and 3105 cm^{-1} band is due to C-H stretching of aromatic ring . The absorption band at 1605 cm^{-1} indicates the presence of C=C stretching in benzene ring. ^{1}H NMR data - (ppm, 300MHz,TMS)-7.2 (m, Ar-H), 2.5 (s, CH_3), 8.5 (s, 1H).

Compound (4f-ac): Infrared spectrum (cm-1 , KBr) –Absorption at 1590 cm^{-1}due to H-N-H Bending, absorption at 1550cm^{-1} due to N-N, absorption at 1100cm^{-1} due C-N group, absorption at 1675cm^{-1} due to C=C stretching. Absorption at 1575 cm^{-1} due to C-C group. ^{1}H NMR data - (ppm, 300MHz,TMS)-7.2(m, Ar-H), 4.4 (s, NH_2), 9.5 (s, NH)

Compound(4f-ad): Infrared spectrum (cm-1 , KBr) –Absorption at 1590 cm^{-1}dueto H-N-H Bending, absorption at 1550cm^{-1}due to N-N, absorption at 1100cm^{-1} due C-N group, absorption at 1625 cm^{-1} due to C=N group, absorption at 1675cm^{-1} due to C=C stretching. Absorption at 1575 cm^{-1} due to C-C group. ^{1}H NMR data - (ppm, 300MHz,TMS)-7.2(m, Ar-H), 9.5 (s, NH), 2.5 (s, C-H)

RESULTS AND DISCUSSION

3(2-aryl methylidene hydrazinyl)-2H-Chromene-2-one (4f-ad) wereformed2-oxo-2H-chromen-3yl-acetate (4f-ab) and 3-hydrazinyl 2H-Chromene-2-one(4f-ac).All the synthesized compounds characterized by spectral data.

In IR spectra, absorption at 3105 cm^{-1}and1605 cm^{-1}due to C-H and C=C stretching, absorption at 1685 $cm^{-1}$is due to –C=O Group supporting the formation of compound (4f-ab),absorption at 1590 $cm^{-1}$and 1550cm^{-1}due to H-N-H Bending and N-N group supporting the formation of compound(4f-ac), absorption at 1625 cm^{-1} due to C=N group supporting the formation of compound(4f-ad). **In NMR spectra**, signal at 4.4 (s, NH_2), 9.5 (s, NH) supporting the formation of compound (4f-ac), signal at 2.5 (s, C-H) supporting the formation of compound (4f-ad). The details of some of the representative compounds formula, molecular weight, melting point % yield of each compound is given in the table 1.

Table 1

S.No	COMPOUND	MOLECULAR FORMULA	MELTING POINT	MOLECULAR WEIGHT	YIELD %
1.	4f-ad	$C_{11}H_8O_4$	92–94°	204	70
2.	4f-ac	$C_9H_8O_2N_2$	88-90°	176	72
3.	4f-ad	$C_{16}H_{12}O_2N_2$	110-112°	264	67

CONCLUSIONS

This report easy, a simple and convenient route for the synthesis of novel series of 3(2- aryl methylidene hydrazinyl) - 2H-Chromene-2-one.

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