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SEVERAL POSSIBLE ROUTES LEADING TO THE PRODUCTION OF CARBOXYLIC ACID STARTING FROM BENZOPYRONE METHYL KETONE

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ABSTRACT: Derivatives of 3-acetyl coumarin are the essential synthons that are required for the synthesis of a large variety of heterocyclic compounds. Since benzopyran derivatives have such a broad range of uses in medicine, research, food technology, and material science, there are a large variety of methods that may be used to synthesis benzopyrone heterocyclic derivatives. This article describes the synthesis of an oxidative product beginning with a methyl ketone chemical and ending with a haloform reaction. It also confirms the molecular structure of the result. The primary objective of the article is to devise risk-free methods for producing the required compounds, such as carrying out the reaction at room temperature, under reflux circumstances, or in a water bath, with the predicted amount of product. Studies on optimising the solvent and the catalyst were carried out in order to increase the product yield and to initiate the reaction in a manner that was environmentally responsible. In addition, substances are validated by the use of spectroscopic analytical techniques including 1H NMR, 13C NMR, IR, and HRMS spectroscopy. This paper sets the path for researchers to investigate these analogues in order to investigate a wide variety of medical uses.
Keywords : Methyl ketone, haloform reaction, multi-dimensional synthesis, phase transfer catalyst, and benzo-pyrone are some of the keywords that may be found here.

I.INTRODUCTION:

The results of plant extraction include coumarin and its derivatives, and 3-acetyl-2H-chromen-2-one is the starting material for the synthesis of several heterocyclic compounds. There are several publications available to help you learn how to effectively use 3-acetyl-2H-chromen-2-one. From 3-acetyl-2H-chromen-2-one, heterocyclic compounds such as pyridine derivatives, which are used to measure iron by spectrometry, quinolone derivatives with antibacterial and antifungal properties, chalcones, dihydro pyridine carbonitriles, and pyramidines, among others, are created. Fig. 1 illustrates the essence of the chemical modification of 3-acetyl Coumarin.

Haloform reactions were first studied in the year 1822. The halogenation of methyl ketone with hypobromite or hypochlorite, the haloform reaction of methyl ketone with bromine in water in the presence of 1,3-dioxane, the iodoform reaction by treating iodine dissolved in potassium iodide, the Br2 dissolved in water7 in presence of sodium hydroxide, the Aston et al. reported haloform reaction with of sodium hypo sodium hypochlorite and haloform reaction in phase

Advanced haloform reactions16, pentafluoro enolates of aldehydes and ketones, chloral with calcium hydroxide, iodine dissolved in sodium hydroxide, and transfer catalysis are just a few examples of haloform reactions. The stability of the coumarin lactone ring in the presence of base is being sought for in order to carry out the haloform reaction in the presence of alkali. Noster et al. reported17 that 20% NaOH aqueous solution would not cleave the lactone ring after analysing reaction circumstances in terms of alkali concentration screening.

In addition, researchers are looking into the biological significance of 3-acetyl coumarin, which has been shown to be effective in demonstrating anti-fungal activity, anti-tumor activity, cytotoxic action against certain cell lines, anti-bacterial, anti-oxidant, and neuroprotective capabilities. Figure 2 illustrates the consolidation of various methods for converting

methyl ketones into haloform.

The anti-microbial activity of 3-acetyl coumarin against B. Pumilis, B. Subtilis, E. Coli, A. Niger, and R. Oriza was described by Rajendra Prasad et al.25.

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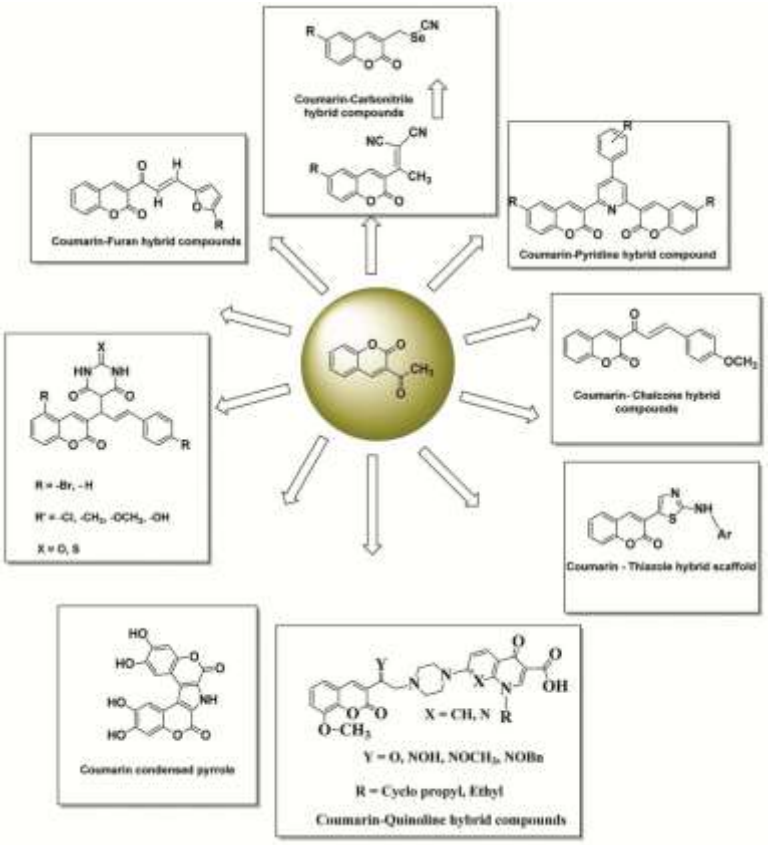

Fig. 1 — Assortment of chemical modifications of 3-acetyl coumarin employed as a key synthon

Rajesh *et al*. reported[26] the synthesis and anti-microbial activity against Staphylococcus Aureus and Staphylococcus pyogenic. Anees *et al*. reported[27] the synthesis and evaluation of *in vitro* anti-hepato carcinoma activity of 3-acetyl coumarin derivatives and their DNA protein binding properties.

Based on all the keen literature survey on the 3-acetyl-2*H*-chromen-2-one in terms of its applications in synthetic organic chemistry as a useful synthon for various heterocyclics, exploration studies of biological activity review, it is taken as research objective and performed haloform reaction of the 3-acetyl-2*H*-chromen-2-one. Though there are lot many methods to synthesize coumarin based carboxylic acid derivatives but no report was found on haloform reaction of 3-acetyl coumarin to subsequent carboxylic acid. Being the method of synthesis chosen is laboratory viable, feasible, single step with green chemistry protocols; this method of synthesis is the profitable path way in terms of product yield, reaction times and quality of the product. This article also emphasizes the reaction optimization studies, method development for the sustainable synthesis of the title compound.

Experimental Details

Melting points were determined from digital melting point apparatus, TLC analysis of the compounds was carried by Aluminium foil coated with silica gel-G supplied by Akshaya company, TLC plates were monitored under UV lamp. ^{1}HNMR spectra were recorded in DMSO-D_6 solvent using TMS as an internal standard compound at 400 MHz frequency. High resolution mass spectra were recorded on Agilent-LCMS instrument. Infrared spectras were recorded on Brooker-FTIR instrument.

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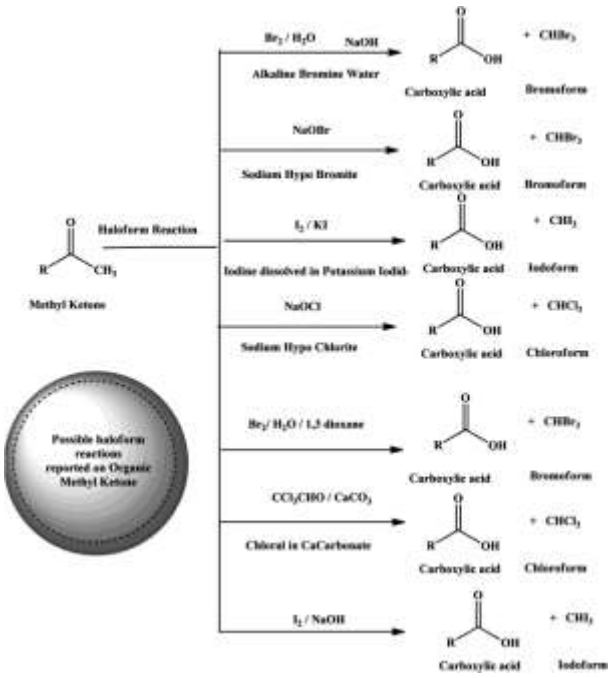

Fig. 2 — Collation of reported haloform reactions on Organic methyl ketones

recorded on Agilent-LCMS instrument. Infrared spectras were recorded on Brooker-FTIR instrument.

Synthetic procedure for the preparation of target compounds

Synthesis of 6-bromo-2-oxo-2H-chromene-3-carboxylic acid from 3-acetyl-6-bromo-2H-chromen-2-one with tetrabutyl ammonium tri bromide (TBATB) as brominating agent (2c)

Equimolar ratio (1:1) of 3-acetyl-6-bromo-2*H*-chromen-2-one and tetra butyl ammonium tribromide (TBATB) were dissolved in ethanol taken in round bottom flask, catalytic amount of 3 M phase transfer catalyst tetra butyl ammonium bromide (TBAB) solution was added reaction was stirred at room temperature for 60 min. Completion of the reaction was preliminarily identified by TLC in chloroform mobile phase under short length UV light.

Synthesis of 6-bromo-2-oxo-2H-chromene-3-carboxylic acid from 3-acetyl-6-bromo- 2H-chromen-2-one with Iodine dissolved in potassium iodide as Iodinating agent (2c)

1 (mmol) of 3-acetyl-6- bromo- 2*H*-chromen-2-onetreated with excess of liquid iodinating agent i.e., solution of I_2/KI in ethanol solvent and added with catalytic amount of 3 M tetrabutyl ammonium bromide and reaction mixture was stirred at RT for 60 min. TLC method is used for the preliminary identification of product formation. Final product formation further confirmed by spectroscopic analysis.

Synthesis of 6-bromo-2-oxo-2H-chromene-3-carboxylic acid from 3-acetyl-6-bromo-2H-chromen-2-one with bromine water (2c)

100 g of 3-acetyl-6-bromo- 2*H*-chromen-2-one was added with excess of bromine dissolved in water and added with catalytic amount of 3 M tetrabutyl ammonium bromide. Furthermore reaction mixture was stirred at room temperature for 60 min of time duration. TLC method is used to identify the completion of the reaction. Products were further confirmed by spectroscopic analysis.

Synthesis of 6-bromo-2-oxo-2H-chromene-3-carboxylic acid from 3-acetyl-6-bromo-2H-chromen-2-one with bromine water under alkaline conditions (2c)

100 g of 3-acetyl-6-bromo-2*H*-chromen-2-one acid was added with excess of bromine dissolved in water and added with catalytic amount of 3 M sodium hydroxide. Furthermore reaction mixture was stirred at room temperature for 4 h. Compound is preliminary identified by the Thin Layer Chromatography. products were further confirmed by spectroscopic analysis.

Synthesis of 6-bromo-2-oxo—2H-chromene-3-carboxylic acid from 3-acetyl-6- bromo-2H-chromen-2-one with TBATB with TBAB (2c)

100 g of 3-acetyl-6-bromo-2*H*-chromen-2-one was added with tetra butyl ammonium bromide (TBATB) and added with catalytic amount of 3 M TBAB. Furthermore reaction mixture was heated on the water bath with shaker for thirty minutes. Further reaction completion primarily identified by TLC in hexane and ethyl acetate mobile phase under UV light. Products were further confirmed by spectroscopic analysis.

Synthesis of 6-bromo-2-oxo—2H-chromene-3-carboxylic acid from 3-acetyl-6- bromo-2H-chromen-2-one with bromine water with TBAB (2c)

100 g of 3-acetyl-6-bromo- 2*H*-chromen-2-one was added with excess of bromine dissolved in water and added with catalytic amount of 3 M TBAB. Furthermore reaction mixture was heated on the water bath on shaker for thirty minutes. Further reaction completion primarily identified by TLC in hexane and ethyl acetate mobile phase under UV light. Products were further confirmed by spectroscopic analysis.

Preparation of reagents

Bromine water solution (Br_2/ H_2O): 25 mL of liquid bromine is dissolved in 500 mL of water. It is

used for the bromination of 3-acetyl coumarin.

Iodine dissolved in Potassium Iodide (I_2 / KI) solution: 3 g of potassium iodide is dissolved in 500 mL of water and 1.5 g of granules of Iodine was added in small lots.

3 M Sodium hydroxide solution (NaOH):60 g of sodium hydroxide dissolved in 500 mL of water to prepare 3M sodium hydroxide solution.

3 M Sodium bi carbonate solution ($NaHCO_3$): 126.03 g of sodium bicarbonate dissolved in 500 mL of water to prepare 3 M sodium bicarbonate solution.

3 M Tetra Butyl Ammonium Bromide (TBAB): 30. 0 g of TBAB dissolved in 31.02 mL of water to prepare 3 M TBAB solution.

3 M Sodium Carbonate (Na_2CO_3) solution: 31.77 g of sodium carbonate dissolved in 100 mL water to prepare 3 M sodium Carbonate.

3 M Potassium hydroxide (KOH) solution: 84.165 g dissolved in 500 mL distilled water to prepare 3 M KOH solution.

TLC mobile phase preparation: Prepared mobile phase with the composition 70: 30 ratio Ethyl Acetate and Hexane.

Tetrabutyl ammonium tribromide solid preparation (TBATB): 9.7 g of tetrabutyl ammonium bromide dissolved in 120 mL water, 3.0 g sodium bromate was added in small lots, drop by drop addition of HBr to the reaction mixture until the solidification is started. Reaction mixture is stirred at room temperature until orange colour solid is developed in RB.

Spectroscopic analysis

2-Oxo-2H-chromene-3-carboxylic acid

Ash colour compound. MF: $C_{10}H_6O_4$,Yield: 3-01 g (95%); MP: 209-211°C (Ethyl Acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR(400 MHz, DMSO-d6 / TMS): δ = 7.42- 7.84 (complex, m, 4 H, Ar-H), 8.55 (s, 1H,Ar-H of lactone ring), 11.0 (s, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 116.1, 118.1, 118.2, 125.4, 127.9, 128.3, 148.5, 153.0, 155.7, 166.2 HRMS calculated for MF: $C_{10}H_6O_4[M+H^+]$: 190.026610 u and observed = 190. 027820 u.

2-Oxo-2H-chromene-3-carboxylic acid

Ash colour compound. MF: $C_{10}H_5BrO_4$, Yield: 2.98 g (94%); MP: 243-245°C (ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarinring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ =7.39- 8.19 (complex, m, 3 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 118.1, 118.8, 119.7, 121.5, 124.9, 130.3, 134.5, 152.0, 155.7, 166.7, HRMS calculated for MF: $C_{10}H_5BrO_4$,$[M+H^+]$: 267.932036 u. and observed = 267.027920 u 7.39- 8.19 (complex, m, 3 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 118.1, 118.8, 119.7, 121.5, 124.9, 130.3, 134.5, 152.0, 155.7, 166.7, HRMS calculated for MF: $C_{10}H_5BrO_4$,$[M+H^+]$: 267.932036 u. and observed = 267.027920 u.

3-Oxo-3H-benzo[f]chromene-2-carboxylic acid

Ash colour compound. MF: $C_{14}H_8O_4$, Yield: 2.98 g (94%); MP: 300-310°C (ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ = 7.42- 8.16(complex, m, 6 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1-H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 115.5, 117.1, 118.6, 122.3, 123.6, 126.5, 128.9, 128.3, 130.1, 130.3, 148.5, 150.0, 155.7, 166.3, HRMS calculated for MF: $C_{14}H_8O_4[M+H^+]$: 240.057175 u.and observed = 240.057950 u.

7-Hydroxy-2-oxo-2H-chromene-3-carboxylic acid

Ash colour compound. MF: $C_{10}H_6O_5$, Yield: 2.98 g (94%); MP: 382-386°C (ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ = 5.35 (s, 1-H, -OH), 6.62- 7.57(complex, m, 3 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1-H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 102.5, 110. 7, 112.1, 130.2, 134.3, 147.6, 157. 3, 158.5, 159.9, 165.3, HRMS calculated for MF: $C_{10}H_6O_5$,$[M+H^+]$: 206.017440 u. and observed = 206. 078960 u.

7-Chloro-2-oxo-2H-chromene-3-carboxylic acid

Ash colour compound. MF: $C_{10}H_5ClO_4$, Yield: 2.98 g (94%); MP: 252-256°C (ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ = 7.36- 8.02
(complex, m, 3 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1-H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 118.5, 123. 7, 126.1, 129.2,
131.3, 134.6, 147. 3, 151.5, 159.9, 165.3, HRMS calculated for MF: $C_{10}H_5ClO_4$,[M+H$^+$]: 223.017440 u. and observed = 223.049760 u.

7-Nitro-2-oxo-2H-chromen-3-carboxylic acid

Ash colour compound. MF: $C_{10}H_5NO_6$, Yield: 2.98 g (94%); MP: 267-269°C (ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ = 7.36- 8.02(complex, m, 3 H, Ar-H), 8.45 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1-H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 118.5, 123. 7, 126.1, 129.2, 131.3, 134.6, 147. 3, 151.5, 159.9, 165.3, HRMS calculated for MF: $C_{10}H_5NO_6$,[M+H$^+$]: 235.017440 u. and observed = 235.048760 u.

8-Methoxy-2-oxo-2H-chromene-3-carboxylic acid: MF

$C_{11}H_8O_5$, MP calculated: 255-256°C.(ethyl acetate): IR (KBr): 1736 cm^{-1} (strong, sharp, -CO- of carboxylic acid); 1614 cm^{-1} (strong, sharp, -CO- of coumarin ring); ^{1}H NMR (400 MHz, DMSO-d6 / TMS): δ = 3.83 (s, 3H, -OCH_3) 7.18- 7.40(complex, m, 3 H, Ar-H), 8.52 (s, 1H,Ar-H of lactone ring), 11.0 (s, 1-H, -COOH hydrogen). ^{13}C NMR (100 MHz, DMSO-d6/ TMS): 55.8, 113.9, 118.5, 120. 7, 121.1, 121.2, 126.3, 140.6, 148.3, 155.5, 166.3, HRMS calculated for MF: $C_{10}H_5NO_6$,[M+H$^+$]:220.017540 u. and observed = 220.058760 u.

Results and Discussions

In continuation to our previous research[28-39], In the initial attempt of haloform reaction, the reaction was started by taking 3-acetyl-6-bromo-2*H*-chromen-2-one (1) and subjected to haloform reactions with various halogenating agents such as bromine water, TBATB and Iodine dissolved in potassium iodide in methanol solvent media with catalytic amount of phase transfer catalyst Tetra Butyl Ammonium Bromide (TBAB) at room temperature reaction conditions in three distinct reaction flasks. Progress of the reaction is monitored by TLC (Scheme 1).

Reaction mechanism of haloform reaction

Haloform reactions are the common identification test for the methyl ketone. Compound **(1)** is treated with halogen and base, methyl ketone is oxidized to the corresponding carboxylic acid under given set of reaction conditions[4] by the formation of haloform as the subsided product (Scheme 2).

Method development

In addition to the above experiment, it is needed to screen the reaction conditions and yield of the product to develop the facile, multi-component, one-pot reaction under benign conditions. Hence, optimization of reaction conditions were carried in terms of time consumption for the completion of the reaction, reaction conditions, catalyst and yield of the product as shown in the Table 1. Column chart of graphical representation of Reaction condition optimization data substantiated in the Fig. 3.

Based on reaction screening and optimization data, it is confirmed that Br_2/ H_2O under alkaline catalytic conditions at running temperature 298 K is sufficient and superior among all for the synthesis of target compound in high yield under green pathway (Scheme 3).

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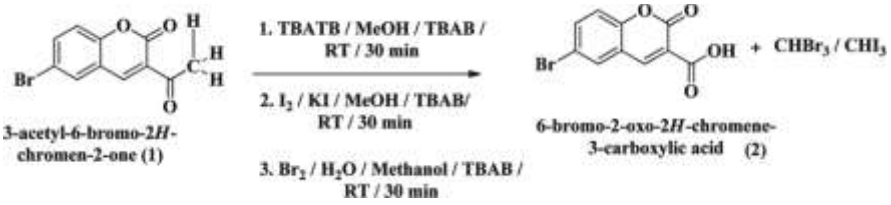
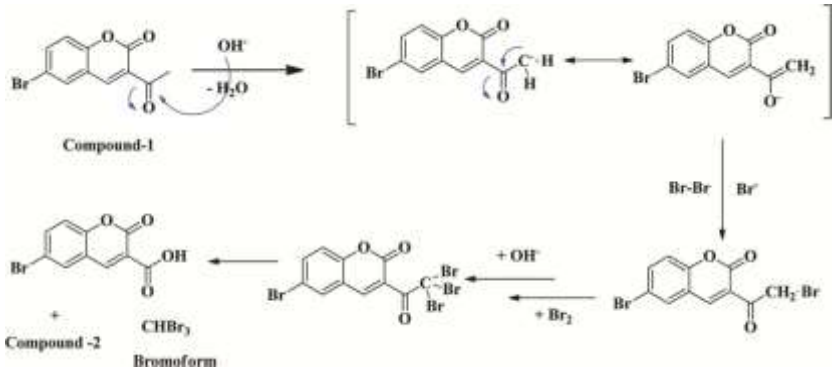


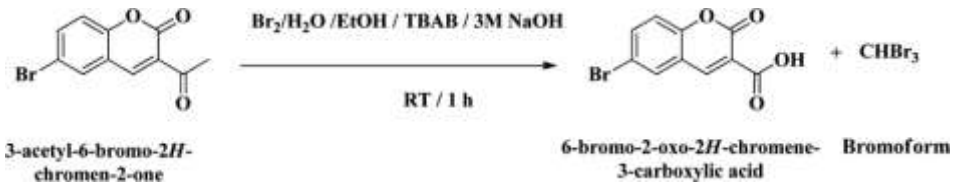
Scheme 1 — Haloform reaction of 3-acetyl-6-bromo-2*H*-chromen-2-one with different halogenating agents



Scheme 2 — Reaction mechanism for the formation of compound (**2**) from compound (**1**)

Table 1 — Optimization of reaction conditions

S. No.	Methyl ketone derivative	Time of the reaction	Reaction conditions	Reagent used	Catalyst	Isolated yield
1	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	TBATB	TBAB	60%
2	3-acetyl-6-bromo-2*H*-chromen-2-one -one	60[1]	RT	I_2/KI	TBAB	50%
3	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	Br_2/H_2O	TBAB	99%
4	3-acetyl-6-bromo-2*H*-chromen-2-one	4 h	RT	TBATB	NaOH	30%
5	3-acetyl-6-bromo-2*H*-chromen-2-one	4 h	RT	Br_2/H_2O	NaOH	98%
6	3-acetyl-6-bromo-2*H*-chromen-2-one	4 h	RT	I_2/KI	NaOH	20%
7	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	TBATB	$NAHCO_3$	NIL
8	3-acetyl-6-bromo-2*H*-chromen-2-one -one	60[1]	RT	I_2/KI	$NAHCO_3$	NIL
9	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	Br_2/H_2O	$NAHCO_3$	NIL
10	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	TBATB	Na_2CO_3	NIL
11	3-acetyl-6-bromo-2*H*-chromen-2-one -one	60[1]	RT	I_2/KI	Na_2CO_3	NIL
12	3-acetyl-6-bromo-2*H*-chromen-2-one	60[1]	RT	Br_2/H_2O	Na_2CO_3	NIL
13	3-acetyl-6-bromo-2*H*-chromen-2-one	30[1]	Water bath	I_2/KI	TBAB	10%
14	3-acetyl-6-bromo-2*H*-chromen-2-one	30[1]	Water bath	TBATB	TBAB	50%
15	3-acetyl-6-bromo-2*H*-chromen-2-one	30[1]	Water bath	Br_2/H_2O	TBAB	70%



Scheme 3 — Haloform reaction of compound (**1**) to yield corresponding carboxylic acid

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Scheme 4 — Accomplishing haloform reaction on compound **1(a-g)** to oxidative product

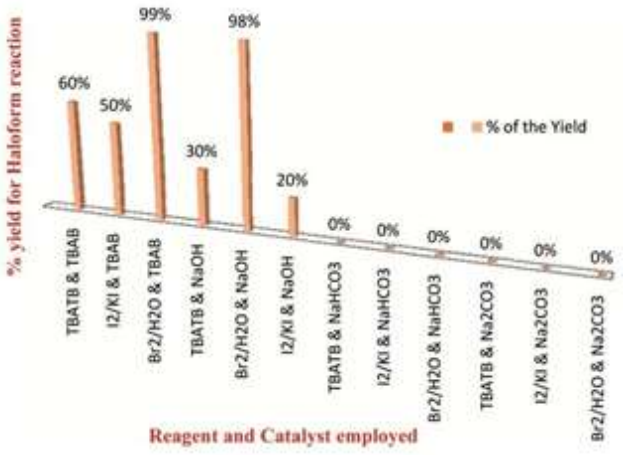

Fig. 3 — ptimization of reaction conditions for haloform reaction of compound (1).

Encouraged with above set of optimized reaction conditions and productivity, this methodology was further extended to various derivatives of the 3-acetyl-2*H*-chromen-2-one (**1**) to perform haloform reaction to achieve the product in excellent yield in short reaction time (Scheme 4)

Conclusion

In conclusion, despite the fact that the haloform reaction is easy and quite frequent in synthetic organic chemistry, a comprehensive search of the literature turned up no reports of the reaction occurring with 3-acetyl coumarin. As a result, the study effort that is being done for this article is focused on completely harmless paths in order to generate the goal chemical.

After a number of failed efforts using a wide variety of catalysts, solvents, and reaction conditions, an effective process for the synthesis of target chemicals was finally developed. It has been discovered that Br2/H2O under alkaline catalytic circumstances and at a running temperature of 298 K is adequate and superior to the other conditions. This was discovered among all of them. As a result, a library of target synthetic similar compounds was manufactured using the approach that was already in place. These synthetic scaffolds are going to become the topic of study in the future, with the goal of expanding specific uses.

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