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SYNTHESIS AND CHARACTERIZATION OF SUBSTITUTED YLIDE CONTAINING COUMARIN DERIVATIVES

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Abstract:

In the present investigation, a series of ylide containing coumarin derivatives were synthesized. The target compound have been achieved through three stages of chemical reactions. In a first stage, three different substituted coumarin derivatives were prepared from condensation between ethylacetoacetate and various substituted phenol derivatives. In a second stage, the substituted coumarin derivatives brominated using N-bromosuccinimide in presence of catalytic amount benzoyl peroxide. In a third stage, bromo substituted coumarin derivatives condensed with triphenyl phosphine yielded as ylide substituted coumarin derivatives. The synthesized compound structures were identified and confirmed by UV-Visible, FT-IR and ^{1}H NMR spectral analysis respectively .

Key Words: Coumarin, NBS, Benzoyl Peroxide, Triphenyl Phosphine & Ylide

1. Introduction:

The attention of organic chemists has been directed towards the field of heterocyclic chemistry, because of their valuable utilities in the synthesis of variety of biologically active derivatives. Coumarins have long been recognized to possess anti-inflammatory, anti-oxidant, anti-allergic, hepatoprotective, anti-thrombotic, anti-viral and anti-carcinogenic activities [4]. In addition to biological activities they are used as additives to food and cosmetics [5] and optical brightening agents [6]. These compounds are involved in the actions of plant growth hormones and growth regulators, the control of the respiration, photosynthesis, as well as defense against infection. Also, they have important effects in plant biochemistry and physiology, acting as antioxidants, enzyme inhibitors and precursors of toxic substances. Coumarins and their derivatives are used in the fields of biology, medicine and polymer science. They are also present or used in perfumes and cosmetics, cigrettes, alcoholic beverages and laser dyes. NBS Bromination is a very important process in organic synthesis as bromo derivatives serve as useful intermediates in the manufacture of pharmaceuticals, agrochemical and other specialist chemicals [21, 22]. Moreover, many pesticides, insecticides, herbicides and fire retardants contain the bromine functionality [23, 24]. Benzylic-methyl group influence of three solvents on the photobromination of picolines was studied. Dichloromethane and benzene were reported as better solvents than the classical solvent carbon tetrachloride. Bromination of toluene type model substrates using NBS and several solvents showed the strong influence of the solvent on the selectivity of the reaction [47, 48] and correlated to the reactivity-selectivity principle [49]. The classical condition for the free radical bromination (NBS/CCl4) of the benzylic methyl group is not optimum due to the high reactivity, resulting a low selectivity. The synthesized compounds were characterized on the basis of UV, FT-IR and ^{1}H-NMR data.

2. Experimental Section:

A. Methods and Materials: The chemicals P-cresol (1), ethylacetoacetate (EAA) (2), NBS (4) and triphenyl phosphine (6), iodine were purchased from Sigma Aldrich, India. Sodiumthiosulphate and ethylalcohol were purchased in quailchem and Hexane, Ethyl acetate, silica gel, and pre-coated thin layer chromatography plates (TLC plates) were purchased from Merck. FTIR spectra were measured using Alpha Bruker FTIR instrument scanning with the entire region of 4000 - 400 cm^{-1} with typical resolution of 1.0 cm^{-1}. UV-Visible spectra were also recorder using Alpha Bruker UV spectrophotometer. The NMR spectra of the compounds have been recorded on Bruker AV400 spectrometer operating at 400 MHz for recording ^{1}HNMR spectra in DMSO solvent using TMS as internal standard. Melting points of all synthesized compounds have been determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected.

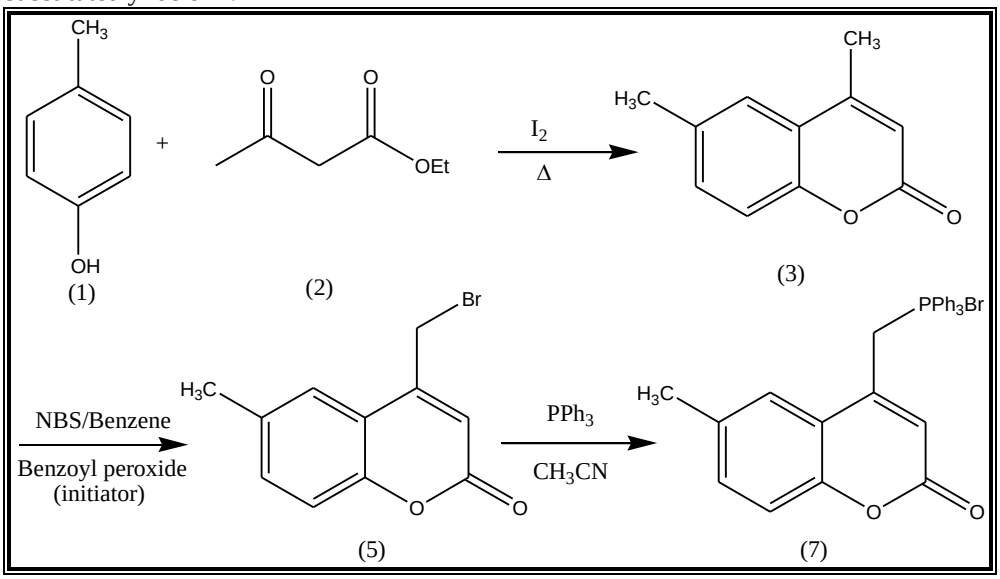
B. Synthesis: The target compound coumarin substituted ylide derivatives [4-((bromo(phenyl)trisphosphino) methyl)-6- methyl-2H- chromen-2-one] were synthesized through three stages.

Stage 1: Synthesis of 4, 6-Dimethyl Coumarin (3) A equimolar mixture of compound 1 (3.15ml, 20mmol), 2 (5.7ml, 20mmol) and iodine (0.025g) was taken in a round bottom flask and dipped in oil bath at 80-85ºC (bath temperature) for an hour. After completion(monitoring by TLC), the reaction mixture was cooled to room temperature and added 6% cold sodium thio sulphate solution and stirred for 10-15 minutes. The precipitated produced and then separated, washed with ice-cold water and recrystallized from hot ethanol to afford get colorless solid of (3).

Stage 2: Synthesis of 4-(bromomethyl)-6-Methyl-2H-Chromen-2-One (5) The pale yellow crystals of 4-(bromomethyl)-6-methyl-2H-chromen-2-one was synthesized by equimolar quantities of (3) (3g, 0.01722mol), (4) (3.065g, 0.01722mol) and benzoyl peroxide (0.05g) placed in round bottom flask equipped with a condenser

at 80ºC under nitrogen atmosphere refluxed overnight. The progress of the reaction was observed by TLC. The reaction mixtures were quenched in to 50ml ice cold water. The reaction mixture was extracted with dichloromethane, the combined organic layer washed with brine solution (2x25ml), dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The fine yellow solid was recrystallized with ethanol.

Stage 3: Synthesis of 4-(bromo(phenyl)trisphosphino)methyl)-6-methyl-2H-chromen-2-one (7) The yellow crystals of compound 5 (1g, 0.00395mol) and 6 (1.036g, 0.00395mol) was dissolved together in acetonitrile (10ml). The solution was stirred overnight at 40ºC. The resulting mixture was concentrated under reduced pressure. The resulting colorless precipitate was recrystallized from toluene methanol (2:1) to yielded as the coumarin substituted ylide of 7.



Scheme: Synthesis of 4-((bromo(phenyl)trisphosphino)methyl)-6-methyl-2H-chromen-2-one (7)

3. Results and Discussion:

Spectral details of 4, 6-dimethyl coumarin (3)

Melting Point	:	175-176ºC	
R_f-value	:	0.95	
UV –Visible (λ_{max}:nm)	:	228 ($\pi \rightarrow \pi^*$ transition), 314 ($n \rightarrow \pi^*$ transition)	
FTIR (cm^{-1})	:	2921 (Aromatic C-H str), 1371(-C-C str.), 1707 (C=O), 1563 (C=C str), 815 (C-H out plane bending	(Figure – 1)
^{1}H NMR (ppm)	:	6.28 (s, 1H, -CH=CH-),7.22-7.38 (m, 3H, Ar-H), 2.44 (s, 6H, CH_3-H)	(Figure – 2)

Spectral details of 4-(bromomethyl)-6-methyl-2H-chromen-2- one (5)

Melting Point	:	185-186ºC	
R_f-value	:	0.79	
UV –Visible (λ_{max}:nm)	:	220 ($\pi \rightarrow \pi^*$ transition), 310 ($n \rightarrow \pi^*$ transition)	
FTIR (cm^{-1})	:	2920 (Aromatic C-H str), 1172 (-C-C str.), 1699 (C=O), 1611 (C=C str), 819 (C-H out plane bending), 920 (-C-Br-str.)	(Figure – 3)
^{1}H NMR (ppm)	:	6.35-6.41 (s, 1H, -CH=CH-),4.81 (s,2H,-CH_2-H) 7.40-7.68 (m, 3H, Ar-H), 2.42 (s, 3H, CH_3-H),	(Figure – 4)

Spectral details of 4-((bromo(phenyl)trisphosphino)methyl)-6-methyl-2H-chromen-2-one (7)

Melting Point	:	196-197ºC	
Rf-value	:	0.67	
UV –Visible (λ_{max}:nm)	:	262 ($\pi \rightarrow \pi^*$ transition), 370 ($n \rightarrow \pi^*$ transition)	
FTIR (cm^{-1})	:	3051 (Aromatic C-H str), 1172 (-C-C str.), 1702 (C=O), 1430 (C=C str), 688 (C-H out plane bending), 920 (-C-Br-str.)	(Figure – 5)
^{1}H NMR (ppm)	:	6.34 (s, 1H, -CH=CH-), 2.93 (s,2H,-CH_2-H) 7.2-7.4 (m, 18H, Ar-H), 2.40 (s, 6H, CH_3-H)	(Figure – 6)

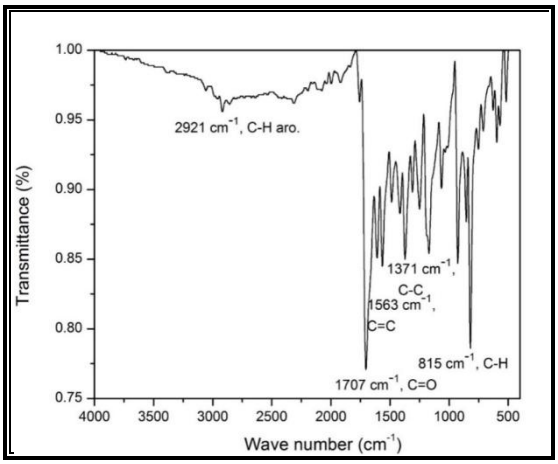


Figure 1: FTIR spectrum compound 3

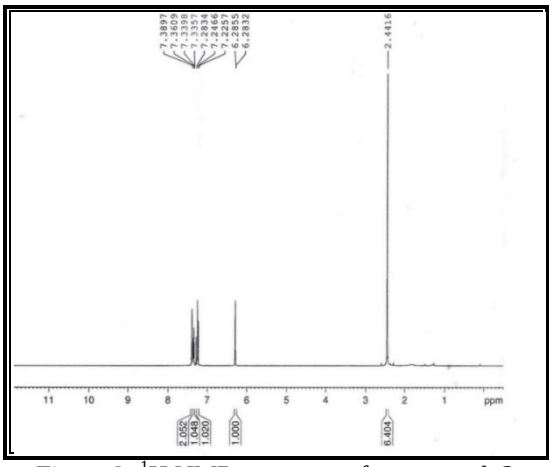


Figure 2: ^{1}H NMR spectrum of compound 3

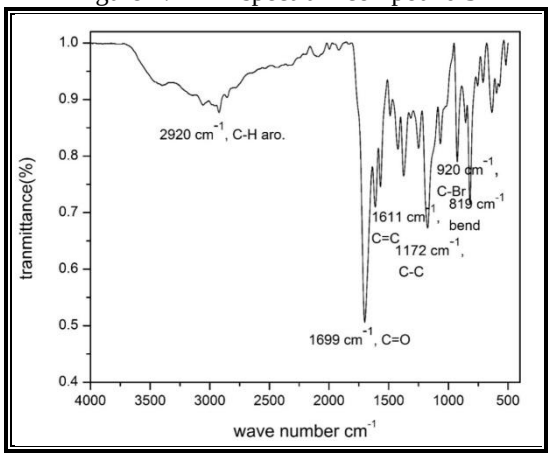


Figure 3: FTIR spectrum compound 5

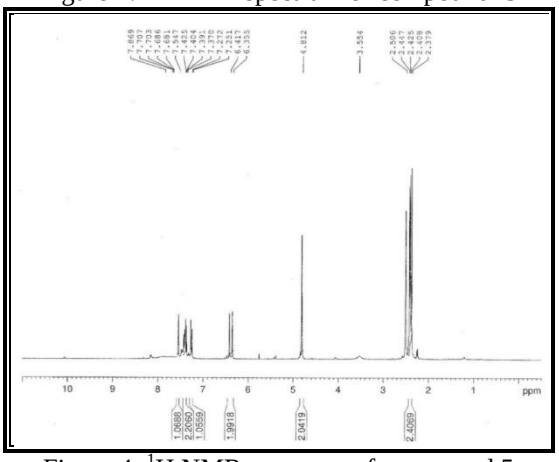


Figure 4: ^{1}H NMR spectrum of compound 5

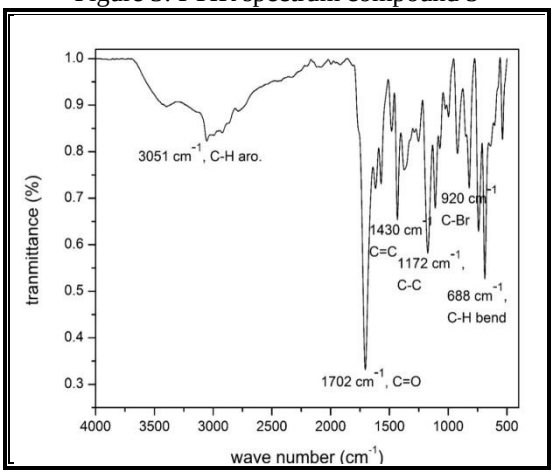


Figure 5: FTIR spectrum of compound 7

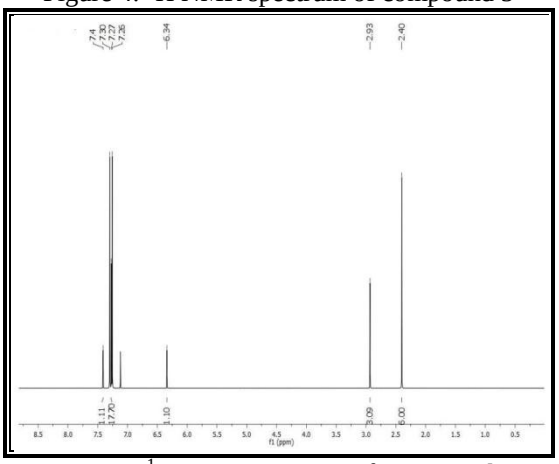


Figure 6: ^{1}H NMR spectrum of compound 7

Figure (1-2) revealed the FTIR and ^{1}HNMR spectrum 4,6-dimethyl coumarin 3 respectively using compound 1 and 2 in the presence of iodine as catalyst has been shown in the scheme. Figure (3-4) revealed the FTIR and ^{1}HNMR spectrum of 4-(bromomethyl)-6-methyl-2H-chromen-2- one (5) respectively using compound 3 and 4 in the presence catalytic amount of benzoyl peroxide has also been presented in the scheme. Figure (5-6) revealed the FTIR and ^{1}HNMR spectrum of 4-((bromo(phenyl)trisphosphino)methyl)-6-methyl-2H-chromen-2-one (7) respectively using compound 5 and 6 with has been shown in the scheme. UV absorption and FTIR spectra of compound (3) has been provided a preliminary idea in confirmation the formation of product. According to the UV spectrum, presence of peaks at 228 and 314 nm clearly showed that the compound (3) has -CH=CH- group respectively. According to the FTIR, represented in Figure (1), presence of peak at 2921, 1371, 1707 and 1563 cm^{-1} have been related to C-H aromatic, C-C, C=O stretching and C=C stretching respectively in the compound 3. Similarly, proton NMR strongly empowered for the formation of the product by its δ value at 6.28, 7.22 – 7.38 and 2.44 ppm corresponding to the –CH=C-, Ar-H and CH_3 protons of compound (3) were mentioned in Figure (2).

UV absorption and FTIR spectra of compound (5) has provided a preliminary idea in confirmation the formation of product. According to the UV spectrum of compound (5), presence of peaks at 220 and 310 nm has been related to aromatic double bond and hetero atom respectively. According to the FTIR, represented in Figure (3), presence of peak at 2920, 1172, 1699, 1611 and 819 cm^{-1} for C-H aromatic stretching, C=C, C=O stretching, C=C, C-H bending vibrations respectively in the compound (6). All such stretching and bending peaks have also been supported for the formation of the product. Similarly, proton NMR strongly empowered for the formation of the product by its δ value at 6.35-6.41, 4.81, 7.40-7.68, and 2.42 ppm corresponding to the C=CH, $-CH_2$, Ar-H and CH_3 protons of compound (5) were mentioned in Figure (4). UV absorption and FTIR spectra of compound (7) has provided a preliminary idea in confirmation the formation of product. According to the UV spectrum of compound (7), presence of peaks at 262 and 370 nm has been related to aromatic double bond and hetero atom respectively. According to the FTIR, represented in Figure (5), presence of peak at 3051, 1172, 1702, 1430 and 920 cm^{-1} for C-H aromatic stretching, C-C, C=O, C=C stretching, C-Br bending vibrations respectively in the compound (7). All such stretching and bending peaks have also been supported for the formation of the product. Similarly, proton NMR strongly empowered for the formation of the product by its δ value at 6.34, 2.93, 7.2 – 7.4 and 2.40 ppm corresponding to the –C=CH, CH_2, Ar-H and CH_3 protons of compound (7) were mentioned in Figure (6). Therefore the synthesized compounds structures were good agreement with the structure of compounds 3, 5 and 7 expected.

4. Conclusions:

In the present investigation of work coumarin bearing ylide derivatives have been synthesized via three stages of chemical reactions. In a first stage, 4,6-dimethylcoumarin have been synthesized in presence of catalytic amount of iodine. Most of the researchers substituted coumarin derivatives have synthesized concentrated sulphuric acid as catalyst. Usage concentrated sulphuric acid is hazardous and dangerous to handle. But iodine as catalyst, very easy to handle, simplified and green chemistry protocol. In the second stage, substituted coumarin derivatives have brominated with N-bromo succinimide in the presence of benzoyl peroxide. In a third stage, methyl brominated compounds reacted with triphenyl phosphine to produced coumarin substituted ylide derivatives. The substituted coumarin ylide derivatives served as very good synthon for synthesizing various oligomers. The chemical structures of compounds **3, 5** and **7** have been confirmed using various spectral techniques viz., FTIR, UV-Visible, and ^{1}H-NMR spectra and were found to be in agreement with the chemical structures expected.

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