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Application of Triphenylphosphine for Facile Synthesis of Several Alkyl Acrylates from Heterocyclic Phenols

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Abstract

7-Hydroxycoumarine undergoes a smooth reaction with alkyl propiolates in the presence of triphenylphosphine (15 mol%) to produce the corresponding alkyl (E)-3-((2-oxo-2H-chromen-7-yl)oxy)acrylate in good yields. When the reaction was performed by 3-hydroxyquinoline similar alkyl acrylates were obtained.

Keywords: *Heterocyclic phenols, 7-hydroxycoumarine, 3-hydroxyquinoline, Aryl vinyl ethers, Alkyl propiolates, Triphenylphosphine.*

Introduction

These years the use of multicomponent reaction has emerged as one of the powerful and efficient tools for the synthesis of structurally diverse molecules and many newly designed d multicomponent reactions have been successively reported [1, 2]. On the other hand the addition of aliphatic or aromatic phenol to the activated alkynes results in an active intermediate vinyl ester, which is an important synthetic building block for the synthesis of a wide variety of heterocycles and pharmaceutical compounds [3, 4].

A number of multicomponent reactions have been developed by using this kind of vinyl ester esters to react further with sequential adding of nucleophilic or electrophilic reagents to give versatile oxygen containing compounds and N,O-heterocycles [5-12]. We also successfully reported several new multicomponent reactions by using of heterocyclic phenols with electron-deficient alkynes such as di alkyl acetylenedicarboxylate and alkyl propiolate [13-18]. We noted that the aryl vinyl ethers derived from the reactions of OH-acids with dialkyl acetylenedicarboxylate and alkyl

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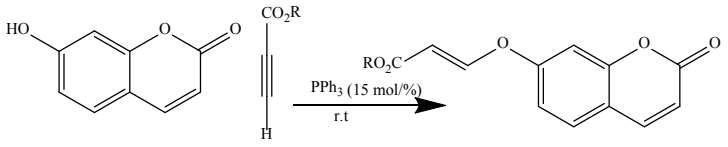
propiolate showed very different reactivity and therefore different reaction patterns were usually encountered [19]. In continuation of our current interest in the application of triphenylphosphine and activated acetylenes in organic synthesis, we report here a simple one-pot synthesis of functionalized aryl vinyl ether derivatives 3 (scheme 1).



3	R	yeild %
a	Me	87
b	Mt	84

Scheme 1. Typical procedure for compound 3.

Experimental

General

IR spectra were measured with a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C spectra were determined on a Bruker DRX-300 Avance instrument in $CDCl_3$ at 300 and 75 MHz, respectively, with δ in ppm and J in Hz. EI mass spectra (70 eV) were measured on a Finnigan-MAT-8430 mass spectrometer. ^{1}H and ^{13}C NMR spectra were obtained from solutions in $CDCl_3$ using TMS as internal standard. All the chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

General procedure for the preparation of compounds **3**

To a stirred solution of Ph_3P (0.052 g, 2 mmol) and **1** (2 mmol) in 10 mL of CH_2Cl_2 was added, drop wise, a mixture of **2** (2 mmol) in 4 mL of CH_2Cl_2 at -5 ºC over 10min. The reaction mixture was then allowed to warm up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the oil products were purified by preparative TLC on silica gel (Merck silica gel DC Fertigplatten 60/Kiesinger F254) 20•20 cm plates using nhexane- EtOAc (2:1) as eluent.

*Methyl (E)-3-((2-oxo-2H-chromen-7-yl)oxy) acrylate (***3a***)*

Yellow oil, yield: 0.38 g (87 %). IR (KBr): υ = 1731 (C=O). ^{1}H-NMR: δ = 3.78 (3 H, s, OCH^3), 5.74 (1 H, d, ^{3}J 12.1 Hz, CH), 6.40 (1 H, d, ^{3}J 9.5 Hz, CH), 7.05 (2 H, m, 2 CH), 7.50 (1 H, d, ^{3}J 8.4 Hz, CH), 7.68 (1 H, d, ^{3}J 9.5 Hz, CH), 7.83 (1 H, d, ^{3}J 12.1 Hz, CH). ^{13}C-NMR: δ = 51.6, 104.2, 105.8, 114.1, 115.6, 115.8, 129.4, 142.7, 155.3, 156.7, 158.2, 160.2, 167.0. MS (EI, 70 eV): m/z (%): 246 (M^+, 20), 83 (87), 59 (40), 39 (75).

*Ethyl (E)-3-((2-oxo-2H-chromen-7-yl)oxy) acrylate (***3b***)*

Yellow oil, yield: 0.43 g (84 %). IR (KBr): υ = 1734 (C=O). ^{1}H-NMR: δ = 1.26 (3 H, t, ^3J 7.1 Hz, CH^3), 4.25 (2 H, q, ^3J 7.1 Hz, OCH^2), 5.72 (1 H, d, ^3J 12.1 Hz, CH), 6.40 (1 H, d, ^3J 9.5 Hz, CH), 7.05 (2 H, m, 2 CH), 7.51 (1 H, d, ^3J 8.4 Hz, CH), 7.69 (1 H, d, ^3J 9.5 Hz, CH), 7.83 (1 H, d, ^3J 12.1 Hz, CH). ^{13}C-NMR: δ = 14.5, 60.7, 104.6, 105.7, 114.3, 115.5, 115.5, 129.1, 142.4, 155.3, 156.3, 158.0, 160.6, 167.3. MS (EI, 70 eV): *m/z* (%):260 (M+, 4), 164 (100), 120 (25), 96 (23), 51 (25).

*Methyl (E)-3-(isoquinolin-3-yloxy)acrylate (***8a***)*

Yellow oil, yield: 0.34 g (75%). IR (KBr): υ = 1731 (C=O). ^{1}H-NMR: δ = 3.80 (3 H, s, OCH_3), 5.74 (1 H, d, ^3J 12.1 Hz, CH), 5.35 (s, 1H), 7.51-7.54 (m, 2H), 8.09 (d, 1H, J 9.1 Hz), 8.70 (d, 1H, *J* 8.3 Hz), 8.82 (br s, 1H), 8.88 (d, 1H, *J* 4.2 Hz), ; ^{13}C NMR: δ = 52.0, 101.6, 108.2, 124.2, 124.8, 125.2, 127.7, 130.8, 137.5, 153.8, 154.3, 166.5, 170.0; Anal. Calcd for $C_{13}H_{11}NO_3$ (229.2): C, 68.11; H, 4.84; N, 6.11; found: C, 68.16; H, 4.82; N, 6.10.

*Ethyl (E)-3-(isoquinolin-3-yloxy)acrylate (***8b***)*

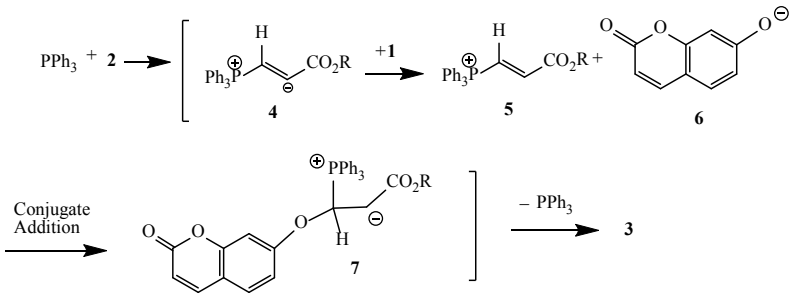
Yellow oil, yield: 0.33 g (68%). IR (KBr): υ = 1735 (C=O). ^{1}H-NMR: δ = 1.33 (3 H, t, ^3J 7.1 Hz, CH_3), 4.28 (2 H, q, ^3J 7.1 Hz, OCH_2), 5.71 (1 H, d, ^3J 12.3 Hz, CH), 5.34 (s, 1H), 7.53-7.52 (m, 2H), 8.06 (d, 1H, J 9.0 Hz), 8.67 (d, 1H, J 8.2 Hz), 8.80 (br s, 1H), 8.87 (d, 1H, J 4.1 Hz), ; ^{13}C NMR: δ = 14.1, 60.6, 101.3, 108.6, 124.7, 124.4, 125.4, 127.5, 130.1, 137.9, 153.8, 154.7, 166.2, 170.3;. Anal. Calcd for $C_{14}H_{13}NO_3$ (243.0): C, 69.12; H, 5.39; N, 5.76; found: C, 69.19; H, 5.31; N, 5.72.

Results and discussion

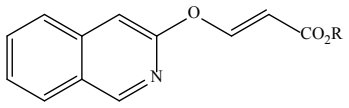
The nucleophilic addition of 7-hydroxycoumarine to alkyl propiolate was carried out under neutral conditions. The reaction of 7-hydroxycoumarine with alkyl propiolate in the presence of Ph3P proceeded spontaneously at room temperature in CH_2Cl_2 and was finished within 24 h. The products were separated by thin-layer chromatography and identified as **3** based on their elemental analyses and their IR, ^{1}H, and ^{13}C NMR spectral data.

The ^{1}H NMR spectrum of **3a** exhibited a single sharp line for the methoxy group at δ = 3.83 ppm, together with an AX system for the trans-olefinic protons at δ = 5.74 and 7.68 ppm with ^3J = 12.1 Hz. The aromatic moiety appeared at δ = 7.40-7068 ppm. The ^{13}C NMR spectrum of **3a** showed thirteen distinct resonances in agreement with the methyl (E)-3-((2-oxo-2H-chromen-7-yl)oxy) acrylate structure. Partial assignments of these resonances are given in the experimental section. The ^{1}H and ^{13}C NMR spectrum of **3b** is similar to those of **3a** except for the alkoxy moieties, which exhibited characteristic resonances with appropriate chemical shifts.

Mechanistically, it is conceivable that the reaction involves the initial formation of a zwitterionic 1:1 intermediate 4 between Ph_3P and the acetylenic compound (Scheme 2) [33]. The intermediate **4** is then protonated by the OH-acidic **1** to afford **5**. The latter might be attacked by the O-atom of the bidentate anion **6** to afford the yields **7**, which is converted to the final product by loss of Ph_3P (Scheme 2). When the reaction is carried out using 3-hydroxyisoquinoline, the same aryl vinyl ethers **8** is obtained in excellent overall yields (Scheme 3). Compounds **8** were identified based on their elemental analyses and their IR, ^1H, and ^{13}C NMR spectral data. Partial assignments of these resonances are given in the experimental section



Scheme 2. A possible mechanism for preparation of 3.



3	R	yeild %
a	Me	75
b	Mt	68

Scheme 3.

Conclusion

We have developed a stereoselective, simple and efficient method for the synthesis of a new family of stable O-aryl vinyl ethers. This method has several advantages such as mild conditions, easy work up, and good to excellent yields for products, which make it attractive for researchers.

Acknowledgements

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