

Triphenylphosphine mediated synthesis of functionalized aryl-vinyl ethers from 7-hydroxy coumarin and methyl acetylene carboxylate

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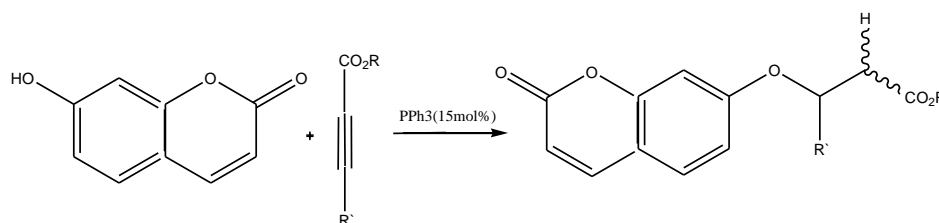
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Abstract- 7-hydroxy coumarin undergoes neutral conditions with alkyl propiolates in the presence of triphenylphosphine, and by the β substitution the corresponding aryl vinyl ethers was obtained in good yields.

Keywords: 7-hydroxy coumarin, aryl vinyl ethers, alkyl propiolates, triphenylphosphine

Introduction

Vinyl ethers of alcohols and phenols are well established monomers building blocks and auxiliaries in organic synthesis, steadily expanding their scope of application [1]. These compounds are important raw materials as practical chemicals for the production of glutaraldehyde as well as vinyl polymer materials containing oxygen, which are expected to degrade easily in nature [2,3]. In this regard; triphenylphosphine has received increasing attention as a versatile and mild reagent in years. We report here a simple one-pot synthesis of functionalized aryl vinyl ether derivatives from 7-hydroxy coumarin and methyl acetylene carboxylates in the presence of triphenylphosphine.



Scheme 1.

Experimental Method

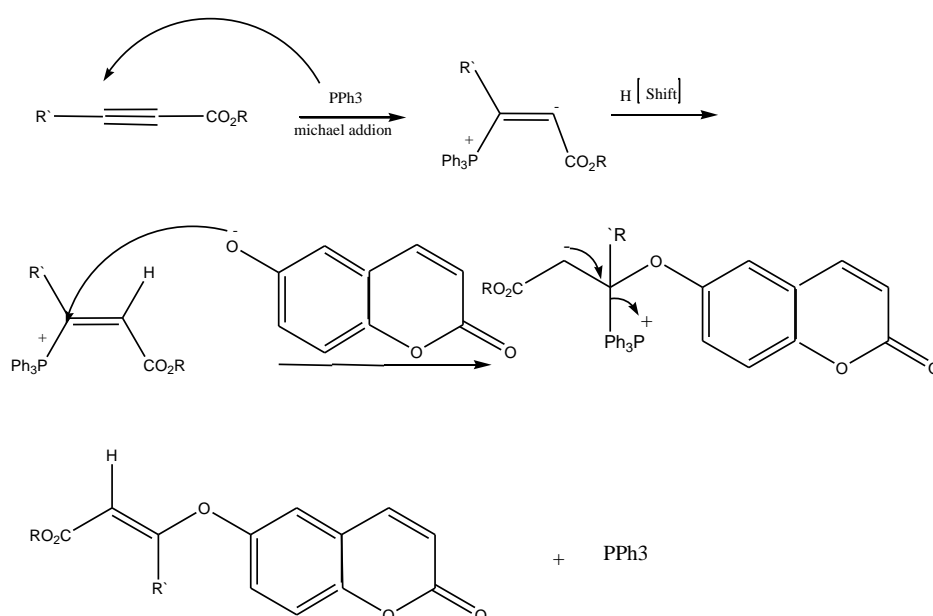
To a stirred solution of 7-hydroxy coumarin (1mmol) in CH_2Cl_2 (5ml) and PPh_3 (1mmol) in 5ml of CH_2Cl_2 , methyl acetylene carboxylate was added.

The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

The solvent was removed under reduced pressure, and the residual was purified by thin layer chromatography using n-hexan_EtoAC (1:1) as eluent.

Results and Discussion

Following nucleophilic PPh_3 attack to (1), through Michael addition intermediate (2) is produced. Then 7-hydroxy coumarin added to intermediate (2) and PPh_3 is removed after twofold bond formation and leads to the formation of the desired product. We anticipate that the reaction described herein represent a simple entry into the synthesis of polyfunctional coumarin derivatives of potential interest. The present method carries the advantage that; not only is the reaction performed under neutral conditions; but also the substance can be mixed without any activation or modification.



Scheme 2.

(a): (2E)-ethyl 3-(2-oxo-2H-chromen-7-yloxy)acrylate

IR (KBR): ν =1735(C=O)esteric.¹H-NMR: δ =7.47(3H, t, CH₃), δ =8.538 (2H, q, CH_{Ar}), δ =12.135(1H, d, CH), δ =9.534 (1H, d, CH_{Ar}) δ = (1H, d, CH_{Ar}), δ = 12.141(1H, d, CH).Anal.Calcd for C₁₄H₁₂O₅: m/e: 260.07 (100.0%), 261/07 (15.5%), 262.08 (1.1%),262.07 (1.0%); C, 64.61; H, 4.65; O, 30.74

(b):(2E)-methyl 3-(2-oxo-2H-chromen-7-yloxy)acrylate

IR (KBR): ν =1735(C=O)esteric.¹H-NMR: δ = 3.78(3H, s, OCH₃), δ =12.132 (1H, d, CH), 9.555(1H, d, CH),7.364 (1H, d, CH_{Ar}),9.54(1H, d, CH), 12.132(1H, d, CH).MS(... eV) m/z (%): 201(100), 77 (61.11), 51(50).Anal.Calcd for C₁₃H₁₀O₅: m/e: 246.05 (100.0%), 247.06 (14.4%), 248.06 (2.0%),262.07 (1.0%); C, 63.42; H, 4.09; O, 32.49

(c): (2Z)-ethyl 3-(2-oxo-2H-chromen-7-yloxy)phenylacrylate

IR (KBR): ν =1735(C=O) esteric. Anal. Calcd for C₁₅H₁₅O₅P: m/e: 306.07 (100.0%), 307.07 (16.6%), 308.07 (2.3%); C, 58.83; H, 4.94; O, 26.12; P, 10.11

The one-pot nature of the procedure makes it an acceptable alternative to multistep approaches. The present coumarin synthesis complements the older established methods and offers significant advantages for the synthesis of coumarin having acid sensitive functional group.

References

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