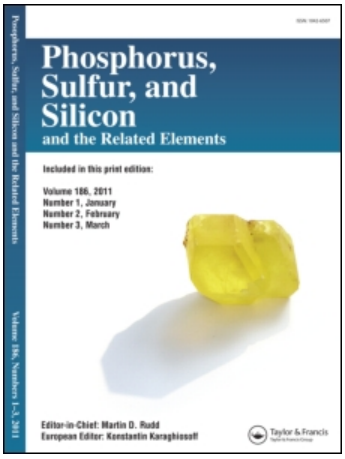

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One-Pot, Three-Component Synthesis of Dialkyl 1,2-Dihydroquinoline-2,3-Dicarboxylates from Triphenylphosphine, Acetylenic Esters, and Amide Derivatives of 2-Aminobenzaldehyde in Aqueous Acetone

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One-Pot, Three-Component Synthesis of Dialkyl 1,2-Dihydroquinoline-2,3-Dicarboxylates from Triphenylphosphine, Acetylenic Esters, and Amide Derivatives of 2-Aminobenzaldehyde in Aqueous Acetone

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by amide derivatives of 2-aminobenzaldehyde in the mixture of acetone-water (3:1) leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce the corresponding stabilized phosphorus ylides. An intramolecular Wittig reaction of the stabilized phosphorus ylide group with the aldehyde group leads to the corresponding dialkyl 1,2-dihydroquinoline-2,3-dicarboxylates.

Keywords 2′-Formylacetanilide; 2′-formylbenzanilide; acetylenic ester; intramolecular Wittig reaction; triphenylphosphine

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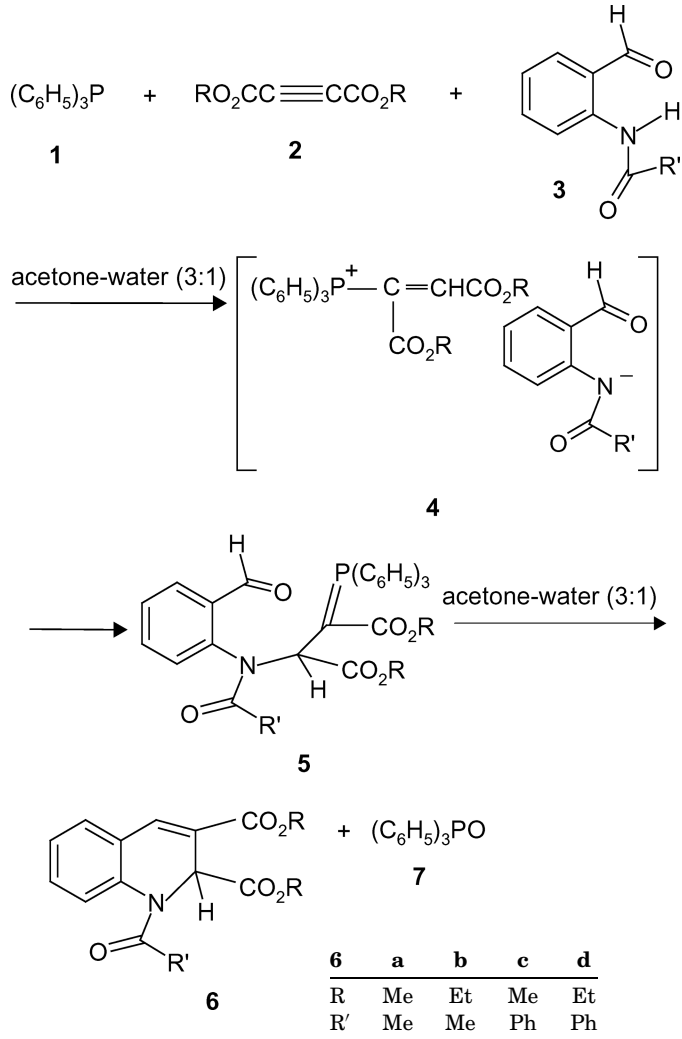
INTRODUCTION

Quinolines are interesting synthetic targets because they act as building blocks for a large number of natural products.[1] In recent years, there has been an increase of interest in the synthesis of quinoline compounds.[1] This interest has resulted from the use of such compounds in a variety of biological and synthetic applications.[1] Organophosphorus compounds have been extensively used in organic synthesis.[2–4] In the past, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[2] In this article, we report on the one-pot synthesis of dialkyl 1,2-dihydroquinoline-2,3-dicarboxylates (**6**) from the reaction of amide derivatives of 2-aminobenzaldehyde (**3**), dialkyl acetylenedicarboxylates (**2**), and triphenylphosphine (**1**) in acetone-water (3:1, Scheme 1).

RESULTS AND DISCUSSION

Several examples are known in which an unsaturated heterocyclic compound is formed from a phosphorane that is connected to a carbonyl group by a chain containing a heteroatom.[1] Thus, quinoline **6** may be considered as the product of an intramolecular Wittig reaction.[1] Such addition-cyclization products apparently result from the initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by attack of the anion of the 2-aminobenzaldehyde derivative **4** on the vinylphosphonium cation **4** to form the phosphorane **5**, which then is converted into quinolines in acetone-water (3:1) with fairly high conversions (Scheme 1). TLC indicated that the reaction was completed after 2 h. The reaction proceeded smoothly and cleanly in an acetone-water (3:1) system at room temperature (in all cases, the reaction works efficiently with fairly high conversions). In dry dichlorometane solvent, these reactions were completed after 24 h.[1] In aqueous media (acetone-water [3:1]), the reactions were completed after 2 h, and also aqueous media systems are very popular from environmentally view points. The structures **6a–d** were deduced from their ^{1}H NMR and ^{13}C NMR spectra and also via an X-ray single crystal (for **6a** and **6c**) structure determination.[5,6] In summary, vinyltriphenylphosphonium salts have been shown to be useful precursors for a new and efficient synthetic route to 1,2-dihydroquinoline derivatives in acetone-water (3:1) system. Other aspects of this process are under investigation.



6	a	b	c	d
R	Me	Et	Me	Et
R′	Me	Me	Ph	Ph

SCHEME 1

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C NMR spectra were measured with a JEOL EX-90A spectrometer at 90 and 22.6 MHz, respectively.

General Procedure for the Preparation of Compounds 6a–d

To a magnetically stirred solution of triphenylphosphine, **1** (1 mmol) and 2-aminobenzaldehyde derivative **3** (1 mmol) in acetone-water (3:1)

(4 mL) was added dropwise to a mixture of **2** (1 mmol) in acetone-water (3:1) (4 mL) at −10 °C over 15 min. The reaction mixture then was allowed to warm to room temperature and was stirred for 2 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using diethyl ether–hexane (1:1) as eluent. The solvent was removed under reduced pressure and products (**6a–d**) were obtained. The characterization data of the compounds (**6a–d**) are given in our previous report (synthesis of dialkyl 1,2-dihydroquinoline-2,3-dicarboxylates for first time in dry dichlorometane solvent. In dry dichlorometane solvent the reactions were completed after 24 h).[1]

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