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NOTE

Triphenylphosphine Catalyzed Stereoselective N-Vinylation of N-(1,3-Dioxo-1,3-dihydroisoindol-2-yl)benzamide

ALI RAMAZANI* and BIJAN GANJEIE
Chemistry Department, Azad University, P.O. Box 45195-467, Zanjan, Iran
E-mail: aliramazani@gmail.com

Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and methyl acetylenecarboxylate by N-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-benzamide leads to vinyltriphenylphosphonium salt, which undergo an addition-elimination reaction in CH_2Cl_2 at room temperature to produce N-vinylated N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide in good yield.

Key Words: Triphenylphosphine, Catalyst, N-vinylation, N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide, Vinyltriphenylphosphonium salt.

β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis[1]. Organophosphorus compounds have been extensively used in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts[2]. A convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts has been established[3]. In this article, the catalytic roll of triphenylphosphine in stereoselective N-vinylation of N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide in good yield is reported (**Scheme-1**).

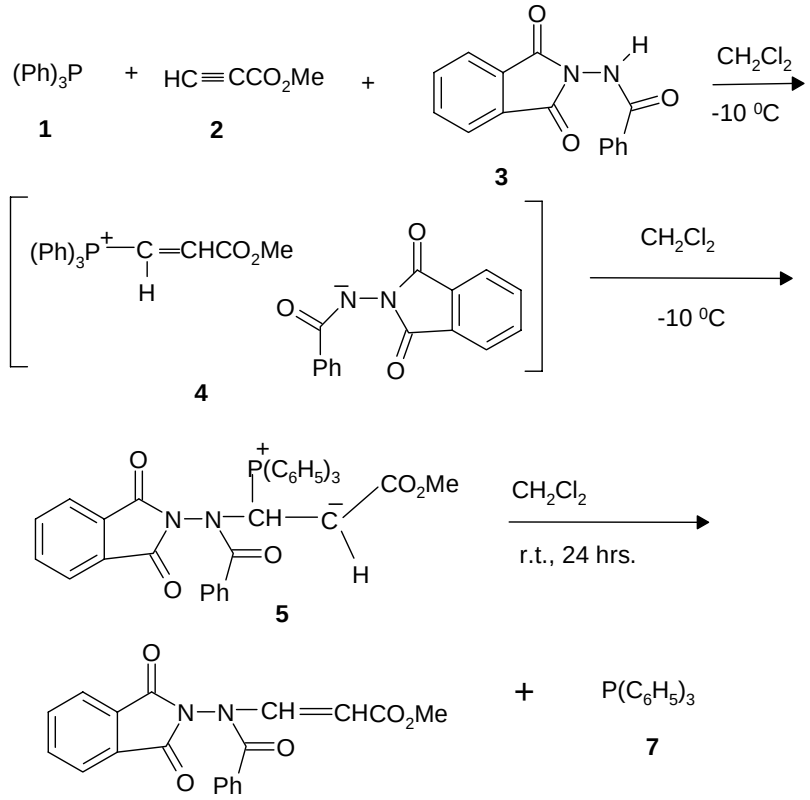
Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively.

Procedure for the preparation of compound 6: To a magnetically stirred solution of triphenylphosphine (**1**) (1 mmol) and N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide (**3**) (1 mmol) in CH_2Cl_2 (6 mL) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (4 mL) at -10ºC over 15 min. The mixture was allowed to warm up to room temperature and stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by silica gel column chromatography using ethyl

acetate-light petroleum ether (1:8) as eluent. The solvent was removed under reduced pressure and products (**6**) were obtained. The characterization data of the compounds (**6**) are given below:

3-[Benzoyl-(l,3-dioxo-1,3-dihydroisoindol-2-yl)amino]acrylic acid (6): Viscous oil, Yield: 40 %; E: 80 %, Z:20 %. IR (KBr, cm^{-1}): 3070 ν(CH, arom); 2954 ν(CH, CH_3); 1743 and 1643 ν(CO, carbonyl); 1288 ν(CO, -OCH_3). ^{1}H NMR ($CDCl_3$) δ_H: 3.38 (CH_3, -OCH_3); 5.20 (1CH, ethylene, d, $^3J_{H-H}$ = 10.8); 7.63 (CH, ethylene, d, $^3J_{H-H}$ = 6.75); 7.38-7.41 and 7.74-7.90 (9 CH, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C : 51.49 (CH_3, -OCH_3); 100.78 (C, ethylene); 123.96-131.47 (C, arom); 134.47 (C, ethylene); 161-165 (4CO, carbonyl).

Preparation of the amide 3[4]: White crystal; m.p.: 307-309ºC; Yield: 70 %. IR (KBr, cm^{-1}): 3470 ν(NH, amide); 1749 and 1670 ν(CO, carbonyl). ^{1}H NMR ($CDCl_3$) δ_H: 7.7-8.2 (CH, m, arom.) 8.1 (NH, amide).



1 **2** **3** **4** **5** **7**

6 : %*E*=80; %*Z*=20

Scheme 1

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts[2,3]. Thus, compounds **6** may result from an initial addition of triphenylphosphine (**1**) to the acetylenic ester (**2**) and

concomitant protonation of the 1:1 adduct by the N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide (**3**) to form the corresponding triphenylphosphonium salt **4**. Conjugate addition of the N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide (**3**) anion to the vinyltriphenylphosphonium cation (**4**) leads to formation of the intermediate **5** which undergo an elimination of triphenylphosphine to produce N-vinylated N-(1,3-dioxo-1,3-dihydroisoindol-2-yl)benzamide in good yield (**Scheme-1**). TLC indicated that the reaction was completed after 24 h in CH_2Cl_2 at room temperature. Other aspects of this process are under investigation.

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