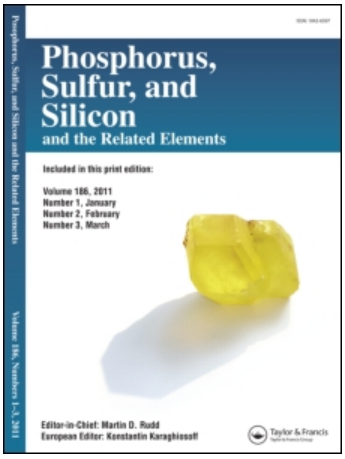

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(*N*-ISOCYANIMINO)TRIPHENYLPHOSPHORANE-CATALYZED STEREOSELECTIVE *O*-VINYLATION OF *N*-HYDROXYIMIDES

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between (*N*-isocyanimino)triphenylphosphorane and dialkyl acetylenecarboxylates, by N-hydroxyimides leads to iminotriphenylphosphorane-containing salts, which undergo a reaction sequence including an addition, a proton transfer, and an elimination to produce the corresponding electron-poor O-vinyl derivatives in high yields under neutral conditions. The reaction is completely stereoselective.

Keywords Acetylenic ester; *N*-hydroxyimide; iminotriphenylphosphorane; (*N*-isocyanimino) triphenylphosphorane; stereoselective

INTRODUCTION

Isocyanide-based reactions have been known about 80 years, with the first described in 1921 and named after its founder, Passerini.[1,2] The chemistry of the isocyanides began in 1859 when Lieke prepared allyl isocyanide as the first isocyanide.[3] Lieke, like many chemists today, was immediately struck by their strange repulsive odor, one of the only negatives of this branch of chemistry. The classical syntheses of isocyanides were developed in 1867 by Gautier.[4] For the following century, only 12 isocyanides were known and rather few types of reactions had been described. Thus for a whole century, from 1859 to 1958, isocyanides were not readily available, and the chemistry of the isocyanides remained an underinvestigated part of organic chemistry.[5–7] In 1921, Passerini pioneered the use of isocyanides and successfully developed a three-component synthesis of α-acyloxycarboxamide by reaction of a carboxylic acid, an aldehyde, and an isocyanide.[1] Today most IMCR (isocyanide-based multi-component reactions) chemistry relates to the classical reactions of Passerini and Ugi. Indeed, the large number of different scaffolds that are now available mostly builds on these two IMCRs and their combination with other types of reactions.[6–28] Passerini reactions involve an oxo-component, an isocyanide, and a nucleophile. Ugi reactions are defined as the reaction of a Schiff base or an enamine

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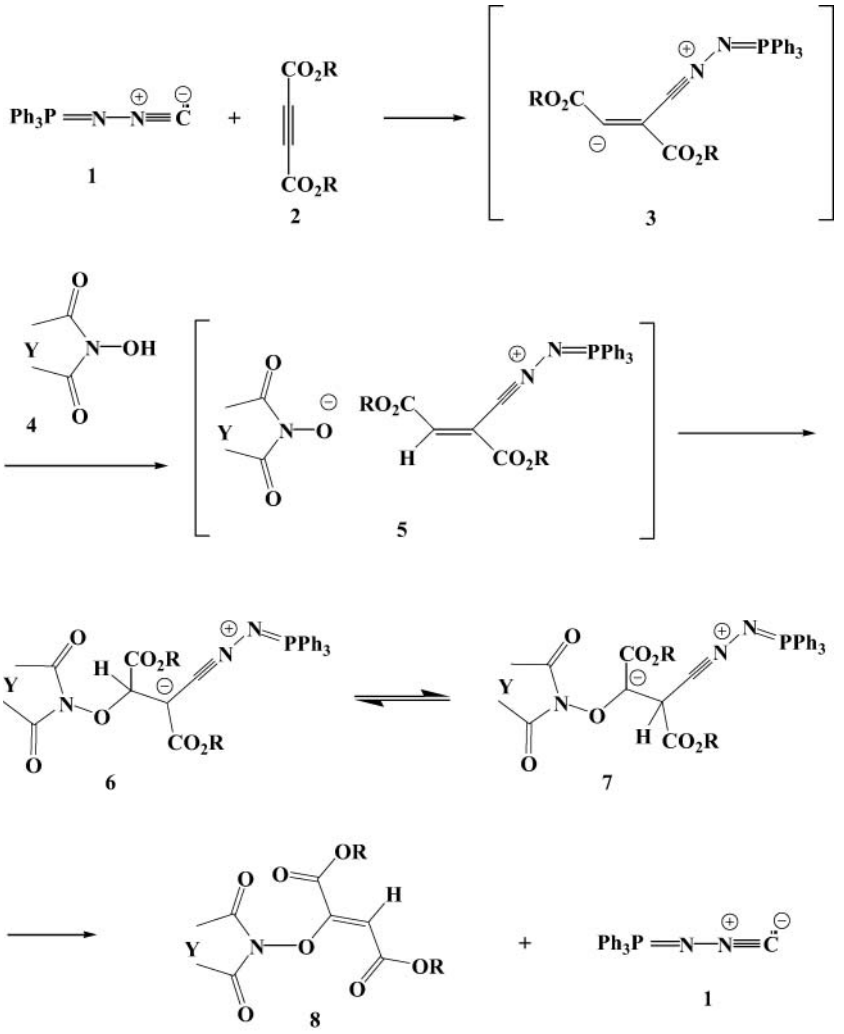
with a nucleophile and an isocyanide, followed by a (Mumm) rearrangement reaction. The Passerini reactions are beginning to find utility in the drug discovery process and in total syntheses of biologically relevant natural products.[7]

Organophosphorus compounds[8–12] have been extensively employed in organic synthesis as useful reagents, as well as ligands, in a number of transition metal catalysts.[8] Iminophosphoranes are a class of a special type of zwitterions, which bear a strongly nucleophilic electron-rich nitrogen. The electron distribution around the P^+–N^- bond and its consequent chemical implications have been probed and assessed through theoretical, spectroscopic, and crystallographic investigations.[13–15] The proton affinity of these iminophosphoranes can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[13–15]

The intramolecular version of the *aza*-Wittig–type reaction has attracted considerable attention recently because of its high potential for the synthesis of a wide variety of nitrogen heterocycles, which can be attributed, in good measure, to the rapid progress in the preparation of functionalized iminophosphoranes. Several interesting heterocyclization reactions involving iminophosphoranes have been reviewed.[13] These compounds can easily be converted through *aza*-Wittig reaction with isocyanates, carbon dioxide, or carbon disulfide into functionalized heterocumulenes, which exhibit a rich chemistry of unusual synthetic promise.[13] The nucleophilicity at the nitrogen is a factor of essential mechanistic importance in the use of these iminophosphoranes as *aza*-Wittig reagents. Iminophosphoranes are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activity.[13] However, the organic chemistry of (*N*-isocyanimino)triphenylphosphorane **1** remains almost unexplored.[26,27] (*N*-isocyanimino)triphenylphosphorane **1** is expected to have synthetic potential because it provides a reaction system in which the iminophosphorane group can react with a reagent having a carbonyl functionality.[26,27] In recent years, we have established a one-pot method for the synthesis of organophosphorus compounds.[16–38] As part of our ongoing program to develop efficient and robust methods for the preparation of heterocyclic compounds (Ali Ramazani reactions),[25–38] we sought to develop a convenient method for the stereoselective *O*-vinylation of *N*-hydroxyimides derivatives **4** in the presence of (*N*-isocyanimino)triphenylphosphorane **1** in high yields under neutral conditions (Scheme 1).

RESULTS AND DISCUSSION

In the last years, several synthetic methods have been reported for the preparation of (*N*-isocyanimino)triphenylphosphorane ($CNNPPh_3$) **1** (Scheme 1).[14,15] There are several reports for the use of (*N*-isocyanimino)triphenylphosphorane **2** in the synthesis of metal complexes.[14,15] However, application of **1** in the synthesis of organic compounds has not been reported. As part of our ongoing program to develop efficient and robust methods for the preparation of heterocyclic compounds,[25–28] we sought to develop a convenient method for the stereoselective *O*-vinylation of *N*-hydroxyimides derivatives **4** in the presence of (*N*-isocyanimino)triphenylphosphorane **1** in high yields under neutral conditions (Scheme 1). Protonation of the highly reactive 1:1 intermediates **3**, produced in the reaction between (*N*-isocyanimino)triphenylphosphorane **1** and dialkyl acetylenecarboxylates **2**, by *N*-hydroxyimides **4** leads to iminotriphenylphosphorane-containing salts **5**, which undergo



Scheme 1 Stereoselective *O*-vinylation of *N*-hydroxyimides.

a reaction sequence including an addition, a proton transfer, and an elimination to produce the corresponding electron-poor *O*-vinyl derivatives **8** in high yields under neutral conditions (Scheme 1). In the reaction, only one stereoisomer (**Z**) was observed as the final product, and therefore, the reaction is completely stereoselective. The reaction proceeds smoothly and cleanly under mild conditions.

A possible explanation is proposed for the formation of **8a–d** in Scheme 1. The structures of the products **8a–d** were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra. The IR spectrum of **8a** showed strong adsorptions at 2997 (CH, aliphatic); 1740 (C=O); 1664 (C=C); 1377 (CH_2); 1273 and 1209 (2 C−O); 1108 (N−O) cm^{-1} indicating the presence of the mentioned functionalities in its formula. The ^{1}H NMR spectrum of compound **8a** exhibited four signals readily recognized as arising from methylene groups

[δ = 2.71 (s, 4 H, CH_2)], methoxy groups [δ = 3.72 and 3.82 (2 s, 6 H, 2 OCH_3)], and a CH of vinylic group [δ = 6.34 (s, 1 H, vinylic)]. The ^{1}H decoupled ^{13}C NMR spectrum of **8a** showed eight distinct resonances [δ = 25.33 (2 CH_2); 52.29 and 53.50 (2 OCH_3); 109.08 (1 CH, vinylic); 149.64 (1 C, vinylic); 160.28 and162.97 (2 C=O of esters) and 169.07 (2 C=O of imides)] that are in agreement with the formula and structure of **8a**. Partial assignment of these resonances is given in the spectral analysis section (see the Experimental section).

CONCLUSION

In summary, we have found a new method for the stereoselective *O*-vinylation of *N*-hydroxyimides derivatives **4** in the presence of (*N*-isocyanimino)triphenylphosphorane **1** in high yields under neutral conditions (Scheme 1). We believe that the reported method offers a mild and simple route for the preparation of these derivatives. Its ease of workup and reaction conditions make it a useful addition to modern synthetic methodologies.

EXPERIMENTAL

^{1}H (250 MHz) and ^{13}C (62.5 MHz) NMR measurements were recorded on a Bruker 250 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. IR spectra were measured on a Shimadzu IR-460 spectrometer. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. (*N*-Isocyanimino)triphenylphosphorane **1** was prepared based on reported procedures.[14,15] Other starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Flash chromatography columns were prepared from Merck silica gel powder.

General Procedure for the Preparation of Compounds 8a–d

To a magnetically stirred solution of (*N*-isocyanimino)triphenylphosphorane,[14,15] **1** (0.302 g, 1 mmol), and *N*-hydroxyimide **4** (1 mmol) in dry CH_2Cl_2 (10 mL), a mixture of dialkyl acetylenecarboxylate **2** (0.10 mL, 1.0 mmol) in dry CH_2Cl_2 (7 mL) at –10 °C was added dropwise over 15 min. The reaction mixture was stirred at the same conditions (–10 °C) for 2 h, and then the mixture was allowed to warm up to room temperature and was stirred for 2 days. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel; petroleum ether:ethyl acetate, 10:2). The solvent was removed under reduced pressure, and the product **8** was obtained. The characterization data of the compounds are given below:

Dimethyl (*Z*)-2-[(2,5-Dioxopyrrolidin-1-yl)oxy]but-2-enedioate 8a. White crystals; mp: 121–122 °C; Yield: 77%. IR (KBr): ν = 2997, 1740, 1664, 1377, 1273, 1209 and 1108 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ_H: 6.34 (s, 1 H, vinylic); 3.82 and 3.72 (2 s, 6 H, CH_3); 2.71 (s, 4 H, CH_2). ^{13}C NMR ($CDCl_3$) δ_C: 169.07 (2 C, C=O of imide); 162.97 and 160.28 (2 C, 2 C=O of esters); 149.64 (1 C, vinylic); 109.08 (1 CH, vinylic); 53.50 and 52.29 (2 CH_3); 25.33 (2 CH_2).

Diethyl (*Z*)-2-[(2,5-Dioxopyrrolidin-1-yl)oxy]but-2-enedioate 8b. White crystals; mp: 115–116 °C; Yield: 71%. IR (KBr): ν = 2992, 1746, 1662, 1377, 1277, 1208 and 1108 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ_H: 6.30 (1 H, vinylic); 4.23 and 4.12 (2 q, 4 H, $^3J_{HH}$ = 7.2 Hz, 2 CH_2 of esters); 2.71 (s, 4 H, 2 CH_2 of ring); 1.27 and 1.23 (2 t, 6 H, $^3J_{HH}$ = 7.2 Hz, 2 CH_3). ^{13}C NMR ($CDCl_3$) δ_C: 169.16 (2 C, C=O of imide); 162.53 and 159.80

(2 C, 2 C=O of esters); 149.74 (1 C, vinylic); 109.31 (1 CH, vinylic); 62.92 and 61.31 (2 CH_2 of ester); 25.32 (2 CH_2 of ring); 14.00 and 13.87 (2 CH_3 of esters).

Dimethyl (*Z*)-2-[(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)oxy]but-2-enedioate 8c. White crystals; mp: 123–124 °C; Yield: 72%. IR (KBr): $\nu = 3008$, 2969, 1746, 1662, 1454, 1292, 1208 and 1100 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H: 7.88–7.86 (m, 2 H, arom); 7.79–7.76 (m, 2 H, arom); 6.43 (s, 1 H, vinylic); 3.83 and 3.71 (2 s, 6 H, CH_3). ^{13}C NMR ($CDCl_3$) δ_C: 163.05, 162.76 and 160.47 (4 C=O); 150.43 (1 C, vinylic); 134.86 (2 CH, arom); 128.68 (2 C, arom); 123.97 (2 CH, arom); 111.16 (1 CH, vinylic); 53.41 and 52.29 (2 CH_3).

Diethyl (*Z*)-2-[(1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl)oxy]but-2-enedioate 8d. White crystals; mp: 114–115 °C; Yield: 70%. IR (KBr): $\nu = 3077$, 2985, 1754, 1669, 1469, 1369, 1277, 1192, 1108, 1031 and 885 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H: 7.90–7.82 (m, 2 H, arom); 7.78–7.72 (m, 2 H, arom); 6.39 (s, 1 H, vinylic); 4.22 and 4.11 (2 q, 4 H, $^3J_{HH} = 7.0$ Hz, 2 CH_2); 1.27–1.19 (m, 6 H, 2 CH_3). ^{13}C NMR ($CDCl_3$) δ_C: 162.64, 161.74 and 159.99 (4 C=O); 150.52 (1 C, vinylic); 134.86 (2 CH, arom), 128.64 (2C, arom), 123.89 (2 CH, arom); 111.20 (1 CH, vinylic); 62.79 and 61.34 (2 CH_2); 14.00 and 13.87 (2 CH_3).

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