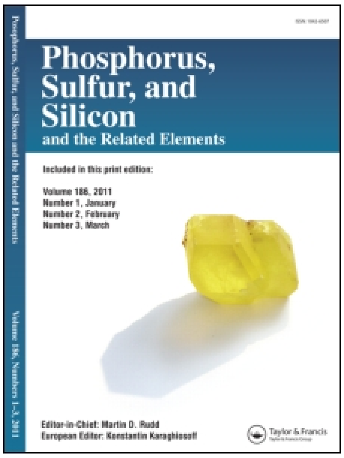

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Tributylphosphine Catalyzed Stereoselective N -Vinylation of Phthalimide and Succinimide

Ali Ramazani[a]; Nader Noshiranzadeh[a]; Bagher Mohammadi[a]
[a] Zanjan University, Zanjan, Iran

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TRIBUTYLPHOSPHINE CATALYZED STEREOSELECTIVE *N*-VINYLATION OF PHTHALIMIDE AND SUCCINIMIDE

Ali Ramazani, Nader Noshiranzadeh,
and Bagher Mohammadi
Zanjan University, Zanjan, Iran

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Protonation of the highly reactive 1:1 intermediates produced in the reaction between tributylphosphine and dialkyl acetylenedicarboxylates by imides (phthalimide and succinimide) leads to vinyltributylphosphonium salts, which undergo an addition-elimination reaction in CH_2Cl_2 at room temperature to produce the corresponding N-*vinylimides (*Z *isomers) in excellent yields.*

Keywords: Acetylenic esters; catalyst; phthalimide; succinimide; tributylphosphine; vinyltributylphosphonium salt

INTRODUCTION

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.[1–9] Organophosphorus compounds have been used extensively in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts.[10] However, there are few reactions in which organophosphorus (III) species work as catalysts.[5,11] In recent years, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilising in situ generation of the phosphonium salts.[2–8] In this article, we wish to report facial one-pot stereoselective synthesis of (*Z*)-*N*-vinylimides **6** in excellent yields (Scheme 1).

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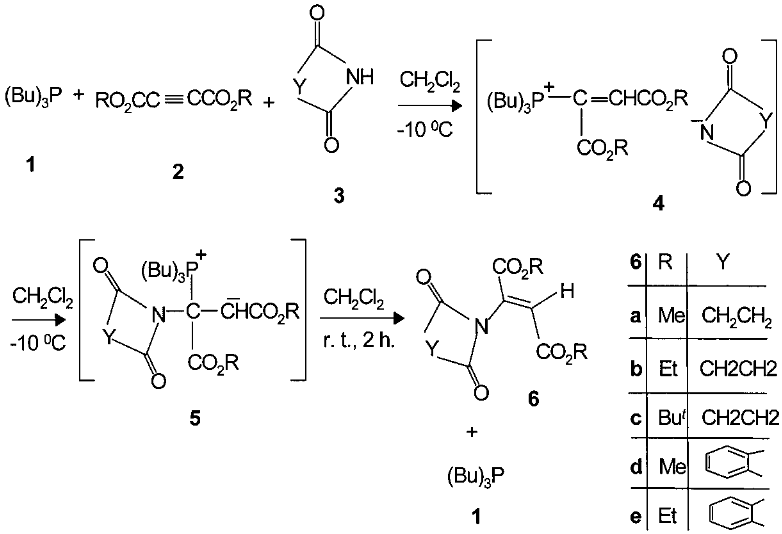
Address correspondence to Ali Ramazani, Chemistry Department, PO Box 45195-313, Zanjan, Iran. E-mail: a-ramazani@mail.znu.ac.ir



6	R	Y
a	Me	CH_2CH_2
b	Et	CH2CH2
c	Bu^t	CH2CH2
d	Me	
e	Et	

SCHEME 1

RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts.[11] Thus, compounds **6** may result from an initial addition of tributylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by the imide (**3**) to form the corresponding tributylphosphonium salts **4**. Conjugate addition of the imide (**3**) anion to the vinyltributylphosphonium cation counterpart followed by elimination of tributylphosphine to be recycled as a catalyst leads to the (*Z*)-*N*-vinylimides **6** as the final product in excellent yields (Scheme 1). In the reaction the mole ratio of reactants (**2** and **3**) and catalyst (**1**) is equal. The reaction proceeds smoothly and cleanly under very mild conditions (in all cases the reaction works efficiently at room temperature and the reaction time is about 2 h) and no side reactions were observed. Reduction of the mole ratio of the tributylphosphine (**1**) relative to the reactants (**2** and **3**) caused a high increase in the reaction time (in case of a 10% molar ratio of catalyst (**1**) relative to the reactants (**2** and **3**), the reaction time is about 72 h). We have also used triethylamine instead of tributylphosphine (**1**) in this reaction, but no corresponding products were observed under the same conditions.

The structures **6a–e** were deduced from their elemental analyses and their UV, IR, ^1H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at *m/z* of 241, 269, 325, 289, and 317 respectively.

In summary, we have developed a convenient, one-pot stereoselective synthesis of (*Z*)-*N*-vinylimides **6** utilising in situ generation of the vinyltributylphosphonium salt **4**. Other aspects of this process are under investigation.

EXPERIMENTAL

Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrophothometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General procedure for the preparation of (Z)-N-vinylimides (**6a–e**): To a magnetically stirred solution of tributylphosphine (**1**) (1 mmol) and imide **3** (1 mmol) in CH_2Cl_2 (7 ml) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (4 ml) at $-10°C$ over 15 min. The mixture was allowed to warm to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel; ethyl acetate-light petroleum ether). The solvent was removed under reduced pressure and the products (**6a–e**) were obtained as the residue. The characterisation data of (*Z*)-*N*-vinylimides (**6a–e**) are given below:

*Dimethyl(**Z**)-2-(2,5-dioxo-1-pyrrolidinyl)-2-butenedioate* (**6a**): Viscous colorless oil. Yield: 95%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 293, 3.48; 242, 2.36. IR (CCl_4) (ν_{max}, Cm^{-1}): 2968, 1734, 1024. ^{1}H NMR ($CDCl_3$) δ_H: 2.86 (4 H, s, CH_2CH_2), 3.74 and 3.83 (6 H, 2 s, 2 OCH_3); 7.08 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 28.91 (CH_2CH_2); 52.44 and 53.44 (2 OCH_3); 128.70 (CH=); 132.66 (N–C=), 161.70 and 162.92 (2C=O of esters); 174.55 (C=O, imide). MS (*m/z*, *%*): 241 (M^+, 23), 209 (28); 182 (100); 180 (28); 154 (10); 149 (7). Found: C, 49.95; H, 4.61; N, 5.75. $C_{10}H_{11}NO_6$ requires C, 49.80; H, 4.56; N, 5.80%.

*Diethyl(**Z**)-2-(2,5-dioxo-1-pyrrolidinyl)-2-butenedioate* (**6b**): Viscous colorless oil. Yield: 96%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 295, 3.55; 210, 4.10. IR (CCl_4) (ν_{max}, Cm^{-1}): 2969, 1737, 1021. ^{1}H NMR ($CDCl_3$) δ_H: 1.28 and 1.32 (6 H, 2 t, $^{3}J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 2.89 (4 H, s, CH_2CH_2), 4.20 and 4.30 (4 H, 2 q, $^{3}J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 7.09 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 13.98 and 13.99 (2 CH_3 of 2 Et); 28.93 (CH_2CH_2); 61.70 and 62.94 (2 OCH_2); 129.09 (CH=); 132.54 (N–C=), 161.32 and 162.66 (2C=O of esters); 174.87 (C=O, imide). MS (*m/z*, *%*): 269 (M^+, 14), 240 (7); 224 (25); 223 (43); 196 (100); 195 (49); 167 (35);

150 (46); 139 (51); 122 (42); 113 (17); 99 (14); 67 (10). Found: C, 53.69; H, 5.65; N, 5.32. $C_{12}H_{15}NO_6$ requires C, 53.48; H, 5.57; N, 5.20%.

*Di-tert-butyl(**Z**)-2-(2,5-dioxo-1-pyrrolidinyl)-2-butenedioate* (**6c**): White crystals; m.p.: 146–148°C. Yield: 98%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 299, 3.31; 214, 3.99. IR (KBr) (ν_{max}, Cm^{-1}): 2971, 1741, 1018. ^1H NMR ($CDCl_3$) δ_H: 1.46 and 1.51 (18 H, 2 s, 2 C $(CH_3)_3$); 2.86 (4 H, s, CH_2CH_2), 6.93 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) δ_C: 27.84 and 27.94 (2 OC $(^{13}CH_3)_3$); 28.86 (CH_2CH_2); 82.57 and 83.85 (2 $O^{13}C$ $(CH_3)_3$); 130.03 (CH=); 132.30 (N—C=), 160.34 and 162.02 (2C=O of esters); 174.61 (C=O, imide). MS (*m/z*, *%*): 325 (M^+, 3), 251 (10); 214 (23); 213 (59); 194 (27); 195 (83); 169 (23); 148 (24); 139 (11); 125 (10); 124 (30); 122 (100); 112 (6); 55 (15). Found: C, 58.89; H, 7.18; N, 4.41. $C_{16}H_{23}NO_6$ requires C, 59.01; H, 7.07; N, 4.30%.

*Dimethyl(**Z**)-2-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)-2-butenedioate* (**6d**): White crystals; m.p.: 104–105°C. Yield: 97%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 395, 2.80; 299, 4.20. IR (KBr) (ν_{max}, Cm^{-1}): 3071, 2961, 1742. ^1H NMR ($CDCl_3$) δ_H: 3.74 and 3.87 (6 H, 2 s, 2 OCH_3); 7.18 (1 H, s, CH=); 7.78–7.82 (2 H, m, arom.); 7.92–7.96 (2 H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 52.45 and 53.49 (2 OCH_3); 128.70 (CH=); 131.73 (C-*ipso*, arom.); 132.09 (N—C=), 124.14 and 134.14 (2CH, arom.); 162.38 and 163.19 (2C=O of esters); 165.54 (C=O, imide). MS (*m/z*, *%*): 289 (M^+, 51), 287 (21), 258 (14); 229 (100); 197 (28); 161 (11); 130 (15); 128 (38), 105 (18); 102 (47); 75 (5). Found: C, 58.29; H, 3.94; N, 4.73%. $C_{14}H_{11}NO_6$ requires C, 58.13; H, 3.83; N, 4.84%.

*Diethyl(**Z**)-2-(1,3-dioxo-1,3-dihydro-2H-isoindol-2-yl)-2-butenedioate* (**6e**): White crystals; m.p.: 81–82°C. Yield: 96%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 397, 2.72; 301, 4.24. IR (KBr) (ν_{max}, Cm^{-1}): 3075, 2960, 1740. ^1H NMR ($CDCl_3$) δ_H: 1.19 and 1.31 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et); 4.16 and 4.31 (4 H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et); 7.15 (1 H, s, CH=); 7.76–7.80 (2 H, m, arom.); 7.90–7.94 (2 H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 13.92 and 14.02 (2 CH_3 of 2 Et); 61.50 and 62.80 (2 OCH_2); 128.68 (CH=); 131.71 (C-*ipso*, arom.); 132.13 (N—C=), 124.05 and 134.52 (2CH, arom.); 161.82 and 162.81 (2C=O of esters); 165.50 (C=O, imide). MS (*m/z*, *%*): 317 (M^+, 19), 316 (10), 271 (43); 245 (81); 243 (100); 217 (22); 215 (36); 200 (12); 198 (38), 173 (13); 170 (25); 148 (31); 147 (42); 129 (19); 104 (17); 103 (36); 76 (4). Found: C, 60.39; H, 4.87; N, 4.30. $C_{16}H_{15}NO_6$ requires C, 60.57; H, 4.76; N, 4.41%.

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