

## Ionic liquids as efficient catalysts for synthesis of phosphorylated dialkyl succinates containing phthalazin-1-one moieties

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### ABSTRACT

Ionic liquids such as 1,3-dialkylimidazolium salts make excellent catalysts and solvents for synthesis of dialkyl 2-(dialkoxyphosphoryl)-3-(1-oxo-1-*H*-phthalazin-2-yl)succinates from 2*H*-phthalazin-1-one, dialkyl acetylenedicarboxylates, and trialkyl phosphites. Under similar conditions, triphenyl phosphite led to dialkyl 2-(diphenoxyphosphoryl)-3-(1-oxo-1-*H*-phthalazin-2-yl)succinates. The ionic liquid was readily recycled and can be reused four times without significant loss of activity or mass.

**Keywords:** Phosphorylation, Organocatalysis, 2*H*-Phthalazin-1-one, Acetylenic ester, Ionic liquid.

### 1. Introduction

Ionic liquids (ILs) are ionic compounds that have a melting point below 100 °C. Most of the commonly used ILs are liquids at room temperature. Ionic liquids have a high polarity (usually between acetonitrile and methanol) and low vapor pressure. These features combined with the fact that most ionic liquids are immiscible with less polar organic solvents led to their use as media or co-solvent in catalysis. The importance of this area is highlighted by the increasing number of reviews and books dedicated to the topic [1-4]. Room temperature ionic liquids (RTILs), especially those based on the 1,3-di-alkylimidazolium salts, have shown great promise as an attractive alternative to conventional solvents [3]. RTILs possess the unique advantages of high thermal stability, negligible vapor pressure, immiscibility with a number of organic solvents and recyclability [1,3].

Organophosphorus compounds, *i.e.* those bearing a carbon atom directly bound to a phosphorus atom, are synthetic targets of interest, not least because of their value for a variety of industrial, biological, and chemical synthetic uses [4,5]. The successful attack by nucleophilic trivalent phosphorus on a carbon center is facilitated when the latter is part of, or conjugated with, a carbonyl group, or when it is part of an unsaturated bond otherwise activated [6-8].

There are many studies on the reaction between trivalent phosphorus nucleophiles and  $\alpha,\beta$ -unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol [8-10].

Herein, we report the results of our studies involving the reaction of zwitterions derived from trialkyl phosphites **1** and dialkyl acetylenedicarboxylates **2** with 2*H*-phthalazin-1-one (**3**), in 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim]CF<sub>3</sub>SO<sub>3</sub>), which constitute a facile one-pot diastereoselective synthesis of dialkyl 2-(dialkoxyphosphoryl)-3-(1-oxo-1-*H*-phthalazin-2-yl)succinates **4** in good yields. Under similar conditions, triphenyl phosphite led to dialkyl 2-(diphenoxyphosphoryl)-3-(1-oxo-1-*H*-phthalazin-2-yl)succinates.

### 2. Experimental

#### 2.1. General

Compounds **1-3** and the ILs were obtained from Fluka and were used without further purification. M.p.: Electrothermal-9100 apparatus. IR Spectra: Shimadzu IR-460 spectrometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra: Bruker DRX-300 AVANCE instrument; in CDCl<sub>3</sub> at 300 and 75 MHz, respectively;  $\delta$  in ppm, *J* in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in *m/z*. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer. The results agreed favorably with the calculated values.

#### 2.2. General procedure for the preparation of compound **4a-4f**

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To a stirred solution of 2*H*-phthalazin-1-one (3, 0.146 g, 1 mmol) and ester 2 (1 mmol) in 2 mL of [bmim]CF<sub>3</sub>SO<sub>3</sub> was added phosphite 1 (1 mmol) at room temperature over 5 min. After completion of the reaction (30 min), as indicated by TLC (EtOAc/*n*-hexane, 2:1), the products were extracted with Et<sub>2</sub>O (2 × 5 mL). The solvent was evaporated under reduced pressure to leave the crude product, which was purified by column chromatography on silica gel and eluted with a mixture of *n*-hexane:EtOAc (3:1) to afford pure product. The IL was recovered by addition of water (5 mL), separated and dried under vacuum. These reactions were performed without any protective atmosphere of inert gas.

#### Selected spectral data

##### Dimethyl 2-(dimethoxyphosphoryl)-3-(1-oxo-1*H*-phthalazin-2-yl)succinate (**4a**):

Colorless powder; m.p.: 144-145 °C; Yield: 0.37 g (92%). IR (KBr):  $\bar{\nu}$  = 1743, 1663 (C=O), 1270 (P=O) cm<sup>-1</sup>. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.63 (3H, d, <sup>3</sup>J<sub>HP</sub> = 10.8 Hz, MeO), 3.69 (3H, d, <sup>3</sup>J<sub>HP</sub> = 10.8 Hz, MeO), 3.71 (3H, s, MeO), 3.87 (3H, s, MeO), 4.34 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 11.2 Hz, <sup>2</sup>J<sub>HP</sub> = 20.4 Hz, P-CH), 6.23 (1H, br s, P-C-CH), 7.72 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH), 7.78 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH), 7.82 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH), 8.2 (1H, s, CH), 8.44 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH) ppm. <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 44.3 (d, <sup>1</sup>J<sub>CP</sub> = 129.8 Hz, P-C), 53.1 (MeO), 53.2 (MeO), 53.5 (MeO), 53.5 (MeO), 60.2 (P-C-C), 126.4 (CH), 127.0 (CH), 127.7 (C), 129.6 (C), 131.9 (CH), 133.6 (CH), 138.1 (CH), 138.6 (CH), 159.4 (C=O), 164.1 (C=O), 167.8 (d, <sup>2</sup>J<sub>CP</sub> = 3.3 Hz, C=O), 169.1 (d, <sup>3</sup>J<sub>CP</sub> = 19.0 Hz, C=O). MS (EI, 70 eV):  $m/z$  (%) = 398 (M<sup>+</sup>, 8), 366 (49), 339 (23), 307 (100), 289 (55), 257 (62), 109 (13) ppm. Anal. Calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>8</sub>P (398.09): C, 48.25; H, 4.81; N, 7.03. Found: C, 47.91; H, 4.87; N, 7.09%.

##### Diethyl 2-(dimethoxyphosphoryl)-3-(1-oxo-1*H*-phthalazin-2-yl)succinate (**4b**):

Colorless oil; Yield: 0.37 g (86%). IR (KBr):  $\bar{\nu}$  = 1664, 1740 (C=O), 1255 (P=O) cm<sup>-1</sup>. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.17 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 1.35 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 3.64 (3H, d, <sup>3</sup>J<sub>HP</sub> = 11.0 Hz, MeO), 3.69 (3H, d, <sup>3</sup>J<sub>HP</sub> = 11.0 Hz, MeO), 4.19 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, OCH<sub>2</sub>), 4.31 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, OCH<sub>2</sub>), 4.32 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz, <sup>2</sup>J<sub>HP</sub> = 20.5 Hz, P-CH), 6.20 (1H, br s, P-C-CH), 7.71 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 7.78 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 7.82 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 8.19 (1H, s, CH), 8.44 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8.0, CH) ppm. <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.8 (Me), 14.0 (Me), 44.5 (d, <sup>1</sup>J<sub>CP</sub> = 129.3 Hz, P-C), 53.4 (d, <sup>2</sup>J<sub>CP</sub> = 5.0 Hz, MeO), 53.5 (d, <sup>2</sup>J<sub>CP</sub> = 5.0 Hz, MeO), 60.2 (P-C-C), 61.8 (OCH<sub>2</sub>), 62.2 (OCH<sub>2</sub>), 126.4 (CH), 127.0 (CH), 127.8 (C), 129.6 (C), 131.9 (CH), 133.5 (CH), 138.4 (CH), 159.4 (C=O), 167.2 (d, <sup>2</sup>J<sub>PC</sub> = 5.3

Hz, C=O), 168.4 (d, <sup>3</sup>J<sub>PC</sub> = 18.5 Hz, C=O) ppm. MS (EI, 70 eV):  $m/z$  (%) = 426 (M<sup>+</sup>, 6), 394 (45), 353 (25), 322 (100), 317 (35), 285 (70), 109 (11). Anal. Calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>8</sub>P (426.12): C, 50.71; H, 5.44; N, 6.57. Found: C, 51.32; H, 5.40; N, 6.64%.

##### Dimethyl 2-(diethoxyphosphoryl)-3-(1-oxo-1*H*-phthalazin-2-yl)succinate (**4c**):

Colorless oil; Yield: 0.35 g (82%). IR (KBr):  $\bar{\nu}$  = 1663, 1744 (C=O), 1250 (P=O) cm<sup>-1</sup>. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.09 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 1.24 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 3.71 (3H, s, MeO), 3.86 (3H, s, MeO), 3.97-4.01 (2H, m, ABX<sub>3</sub>, OCH<sub>2</sub>), 4.03-4.07 (2H, m, ABX<sub>3</sub>, OCH<sub>2</sub>), 4.32 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz, <sup>2</sup>J<sub>HP</sub> = 20.5 Hz, P-CH), 6.25 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz, <sup>3</sup>J<sub>HP</sub> = 7.0 Hz, P-C-CH), 7.70 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, CH), 7.77 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, CH), 7.83 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.4, CH), 8.18 (1H, s, CH), 8.43 (1H, d, <sup>3</sup>J<sub>HH</sub> = 8. Hz, CH) ppm. <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 16.0 (d, <sup>3</sup>J<sub>CP</sub> = 5.8, Me), 16.1 (d, <sup>3</sup>J<sub>CP</sub> = 5.8, Me), 45.0 (d, <sup>1</sup>J<sub>CP</sub> = 129.0 Hz, P-C), 52.7 (MeO), 52.9 (MeO), 60.4 (br s, P-C-C), 63.0 (d, <sup>2</sup>J<sub>CP</sub> = 6.0 Hz, OCH<sub>2</sub>), 63.1 (d, <sup>2</sup>J<sub>CP</sub> = 6.0, OCH<sub>2</sub>), 126.3 (CH), 127.2 (CH), 129.6 (C), 131.8 (C), 133.5 (CH), 138.0 (CH), 138.3 (CH), 159.3 (C=O), 167.9 (d, <sup>2</sup>J<sub>CP</sub> = 6.5 Hz, C=O), 169.0 (d, <sup>3</sup>J<sub>PC</sub> = 18.3 Hz, C=O) ppm. MS (EI, 70 eV):  $m/z$  (%) = 426 (M<sup>+</sup>, 15), 380 (55), 367 (20), 322 (100), 289 (60), 285 (58), 137 (15). Anal. Calcd for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O<sub>8</sub>P (426.12): C, 50.71; H, 5.44; N, 6.57. Found: C, 50.36; H, 5.48; N, 6.65%.

##### Diethyl 2-(diethoxyphosphoryl)-3-(1-oxo-1*H*-phthalazin-2-yl)succinate (**4d**):

Colorless oil; Yield: 0.34 g (75%). IR (KBr):  $\bar{\nu}$  = 1664, 1744 (C=O), 1250 (P=O) cm<sup>-1</sup>. <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.11 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 1.17 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 1.24 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 1.35 (3H, t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, Me), 3.98-4.02 (2H, m, ABX<sub>3</sub>, OCH<sub>2</sub>), 4.02-4.10 (2H, m, ABX<sub>3</sub>, OCH<sub>2</sub>), 4.18 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, OCH<sub>2</sub>), 4.29 (2H, q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, OCH<sub>2</sub>), 4.30 (1H, dd, <sup>3</sup>J<sub>HH</sub> = 11.5 Hz, <sup>2</sup>J<sub>HP</sub> = 20.5 Hz, P-CH), 6.20 (1H, br s, P-C-CH), 7.69 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 7.77 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 7.82 (1H, t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH), 8.18 (1H, s, CH), 8.43 (1H, d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, CH) ppm. <sup>13</sup>CNMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.8 (Me), 14.0 (Me), 16.0 (d, <sup>3</sup>J<sub>CP</sub> = 5.3, Me), 16.2 (d, <sup>3</sup>J<sub>CP</sub> = 5.3, Me), 45.2 (d, <sup>1</sup>J<sub>CP</sub> = 128.8 Hz, P-C), 60.5 (P-C-C), 61.8 (OCH<sub>2</sub>), 62.2 (OCH<sub>2</sub>), 62.9 (d, <sup>2</sup>J<sub>CP</sub> = 6.0 Hz, OCH<sub>2</sub>), 64.0 (d, <sup>2</sup>J<sub>CP</sub> = 6.0, OCH<sub>2</sub>), 126.3 (CH), 127.0 (CH), 127.8 (C), 129.6 (C), 131.8 (CH), 133.4 (CH), 138.2 (CH), 159.3 (C=O), 167.4 (d, <sup>2</sup>J<sub>CP</sub> = 6.0 Hz, C=O), 168.5 (d, <sup>3</sup>J<sub>CP</sub> = 18.5 Hz, C=O) ppm. MS (EI, 70 eV):  $m/z$  (%) = 454 (M<sup>+</sup>, 17), 408 (45), 381 (28), 337 (100), 317 (51), 313 (68), 137 (15). Anal. Calcd for C<sub>20</sub>H<sub>27</sub>N<sub>2</sub>O<sub>8</sub>P (454.15): C, 52.86; H, 5.99; N, 6.16. Found: C, 53.26; H, 6.07; N, 6.22%.

**Dimethyl 2-(diphenoxyphosphoryl)-3-(1-oxo-1H-phthalazin-2-yl)succinate (4e):**

Colorless oil; Yield: 0.44 g (85%). IR (KBr):  $\bar{\nu}$  = 1665, 1743 (C=O), 1249 (P=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 3.74 (3H, s, MeO), 3.90 (3H, s, MeO), 4.67 (1H, dd,  $^3J_{\text{HH}} = 11.5$  Hz,  $^2J_{\text{HP}} = 21.3$  Hz, P-CH), 6.50 (1H, dd,  $^3J_{\text{HH}} = 11.5$  Hz,  $^3J_{\text{HP}} = 6.5$  Hz, P-C-CH), 7.02-7.13 (m, 5H, OPh), 7.2-7.25 (m, 5H, OPh), 7.65 (1H, d,  $^3J_{\text{HH}} = 7.0$  Hz, CH), 7.70 (1H, t,  $^3J_{\text{HH}} = 7.0$  Hz, CH), 7.81 (1H, t,  $^3J_{\text{HH}} = 7.0$  Hz, CH), 8.11 (1H, s, CH), 8.42 (1H, d,  $^3J_{\text{HH}} = 7.7$  Hz, CH) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 45.9 (d,  $^1J_{\text{CP}} = 129.5$  Hz, P-C), 52.6 (MeO), 52.9 (MeO), 60.2 (br s, P-C-C), 120.2 (CH), 120.2 (CH), 125.2 (CH), 125.2 (CH), 125.9 (CH), 126.1 (CH), 127.2 (CH), 127.8 (C), 129.2 (C), 131.8 (CH), 133.4 (CH), 138.5 (CH), 141.2 (C), 142.2 (C), 159.4 (C=O), 167.9 (d,  $^2J_{\text{CP}} = 6.4$  Hz, C=O), 169.0 (d,  $^3J_{\text{CP}} = 18.2$ , C=O) ppm. MS (EI, 70 eV):  $m/z$  (%) = 524 ( $\text{M}^+$ , 14), 430 (48), 465 (30), 383 (40), 372 (100), 289 (53), 235 (20), 71 (17). Anal. Calcd for  $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_8\text{P}$  (522.12): C, 59.77; H, 4.44; N, 5.36. Found: C, 60.14; H, 4.49; N, 5.42%.

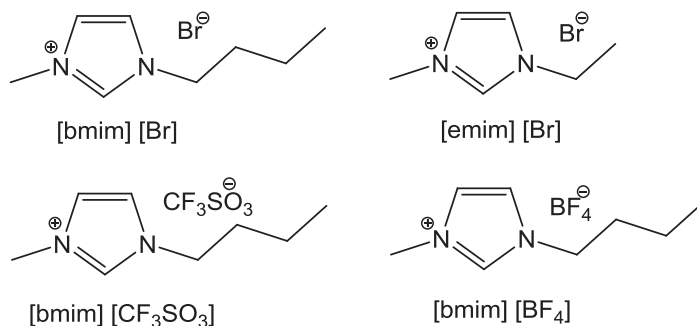
**Diethyl 2-(diphenoxyphosphoryl)-3-(1-oxo-1H-phthalazin-2-yl)succinate (4f):**

Colorless oil; Yield: 0.46 g (83%). IR (KBr):  $\bar{\nu}$  = 1665, 1744 (C=O), 1249 (P=O)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.19 (3H, t,  $^3J_{\text{HH}} = 7.2$  Hz, Me), 1.34 (3H, t,  $^3J_{\text{HH}} = 7.2$ , Me), 4.23 (2H, q,  $^3J_{\text{HH}} = 7.2$  Hz,

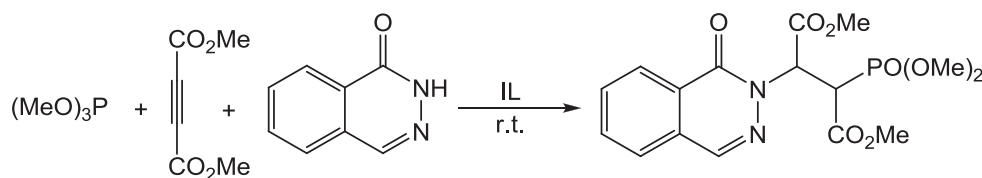
OCH<sub>2</sub>), 4.35 (2H, q,  $^3J_{\text{HH}} = 7.2$  Hz, OCH<sub>2</sub>), 4.64 (1H, dd,  $^3J_{\text{HH}} = 11.1$  Hz,  $^3J_{\text{HP}} = 21.2$  Hz, P-CH), 6.47 (1H, dd,  $^3J_{\text{HH}} = 11.1$  Hz,  $^3J_{\text{HP}} = 6.5$  Hz, P-C-CH), 7.04-7.11 (m, 5H, OPh), 7.20-7.28 (m, 5H, OPh), 7.64 (1H, d,  $^3J_{\text{HH}} = 8.0$  Hz, CH), 7.74 (1H, t,  $^3J_{\text{HH}} = 8.0$  Hz, CH), 7.80 (1H, t,  $^3J_{\text{HH}} = 8.0$  Hz, CH), 8.11 (1H, s, CH), 8.42 (1H, d,  $^3J_{\text{HH}} = 8.0$  Hz, CH) ppm.  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.0 (Me), 14.1 (Me), 46.0 (d,  $^1J_{\text{CP}} = 134.0$  Hz, P-C), 62.2 (OCH<sub>2</sub>), 62.4 (OCH<sub>2</sub>), 60.5 (br s, P-C-C), 120.4 (CH), 120.5 (CH), 125.2 (CH), 125.2 (CH), 125.7 (CH), 125.8 (CH), 126.2 (CH), 127.1 (CH), 127.8 (C), 129.1 (C), 131.8 (CH), 133.5 (CH), 138.5 (CH), 141.2 (C), 141.3 (C), 159.5 (C=O), 167.3 (d,  $^2J_{\text{CP}} = 5.5$  Hz, C=O), 168.5 (d,  $^3J_{\text{CP}} = 18.1$  Hz, C=O) ppm. MS (EI, 70 eV):  $m/z$  (%) = 552 ( $\text{M}^+$ , 17), 479 (28), 458 (50), 410 (63), 386 (100), 317 (40), 235 (27), 71 (15). Anal. Calcd for  $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_8\text{P}$  (550.15): C, 61.09; H, 4.94; N, 5.09. Found: C, 61.46; H, 5.02; N, 5.14%.

**3. Results and Discussion**

Initially, we employed four ILs, shown in Scheme 1, as reaction media and catalysts for phosphorylation reaction. Thus, trimethyl phosphite (**1a**), dimethyl acetylenedicarboxylate (DMAD, **2a**), and 2H-phthalazine-1-one (**3**) were chosen as model compounds for optimization of the reaction conditions. The effects of the type of IL used in the reaction, are investigated. As shown in Scheme 2, [bmim]CF<sub>3</sub>SO<sub>3</sub>



**Scheme 1.** The structures of different ILs used in this study.



IL	Yield/ %
[bmim][Br]	56
[emim][Br]	50
[bmim][CF <sub>3</sub> SO <sub>3</sub> ]	92
[bmim][BF <sub>4</sub> ]	62

**Scheme 2.** The reaction of **1a**, DMAD, and **3** in different ILs as solvent and catalyst.

exhibited better results. When the reactions were carried out in a 1:1 mixture of [bmim]CF<sub>3</sub>SO<sub>3</sub> and H<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub>, the yields were much lower.

The reaction of trialkyl (aryl) phosphites **1** and acetylenic esters **2**, and 2*H*-phthalazin-1-one (**3**) in [bmim]CF<sub>3</sub>SO<sub>3</sub> proceeded smoothly at room temperature and afforded **4a-f** in good yields (Scheme 3). The reactions were complete within 30 min.

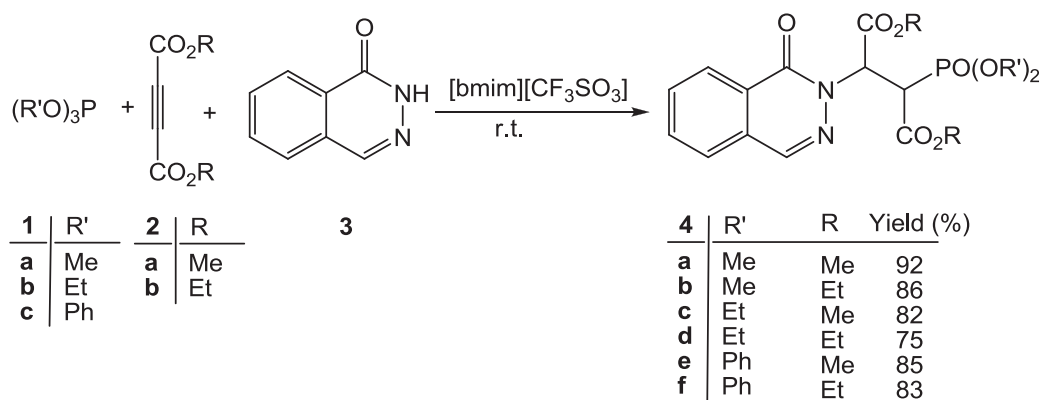
The essential structures of compound **4** were apparent from their mass spectra, which display, in each case, the molecular ion peak at appropriate *m/z* values. The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data, as well as IR spectra, are in agreement with the proposed structures. For example, the <sup>1</sup>H NMR spectrum of **4a** showed two doublets for the two diastereotopic methoxy ( $\delta = 3.63$  ppm, <sup>3</sup>*J*<sub>HP</sub> = 10.8 Hz and  $\delta = 3.69$  ppm, <sup>3</sup>*J*<sub>HP</sub> = 10.8 Hz) groups. The two singlets at  $\delta = 3.71$  and 3.87 ppm belong to the methoxycarbonyl protons. Observation of <sup>3</sup>*J*<sub>HH</sub> = 11.2 Hz for the vicinal methane proton in **4a** indicates the anti arrangement. Since compound **4a** possesses two stereogenic centers, two diastereoisomers with anti-HCCH arrangements are possible (see Experimental).

The presence of <sup>31</sup>P nucleus in compounds **4**, helps in the assignment of the signals by long range couplings with <sup>1</sup>H and <sup>13</sup>C nuclei. The three-bond carbon-

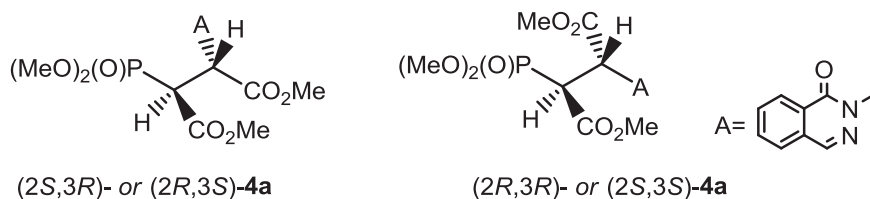
phosphorus couplings, <sup>3</sup>*J*<sub>CP</sub>, depends on configuration, as expected, transoid couplings being larger than cisoid ones. The Karplus relation can be derived from the data for organophosphorus compound with tetra and pentavalent phosphorus [11]. Observation of <sup>3</sup>*J*<sub>CP</sub> = 19.0 Hz for the carbonyl carbon atom of the CO<sub>2</sub>Me group is in agreement with the (2*S*,3*R*)-**4a** or (2*R*,3*S*)-**4a** diastereoisomer (Scheme 4).

Phosphonate ester **4** apparently results from the initial addition of phosphite **1** to the acetylenic ester **2** and subsequent protonation of the 1:1 adduct by the NH-acid **3**. Then, the positively charged ion **6** might be attacked by the conjugate base of the NH-acid to form phosphorane **8**, which is hydrolyzed to the phosphonate ester **4** (see Scheme 5). Hydrolysis of alkyl triphenoxyphosphonium salts in water has been reported to yield diphenyl alkylphosphonates [12]. There are also examples in the literature of the use of methyltriphenoxyphosphonium iodide as a dehydrating agent [12].

The role of the IL may be postulated in terms of some Lewis/Brønsted acidity of the imidazolium cation leading to its interaction with the carbonyl oxygen of the acetylenic ester resulting in its increased polarization and electrophilicity [13]. Thus, promoting the addition and cyclization steps to give product **4** (Scheme 5).



**Scheme 3.** Preparation of compound **4a-f** from phosphites, acetylenic esters, and **3** in [bmim]CF<sub>3</sub>SO<sub>3</sub>.



**Scheme 4.** The diastereoisomers of product **4a**.

