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Synthesis a Novel Class of Unsaturated Cyclic Compounds Containing Phosphorus Atom Using Pseudo Four-Component Condensation Reactions

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A novel pseudo four-component condensation reaction for the efficient synthesis of 2λ^5-[1,2]oxaphosphinin compounds using triphenylphosphine and ethyl bromoacetate in the presence of electron-deficient acetylenic esters without using any catalyst and activation is reported. Fully functionalized 2λ^5-[1,2]oxaphosphinin derivatives can be prepared from simple and readily available precursors under neutral conditions.

Keywords: Ethyl bromoacetate, 2λ^5-[1,2]Oxaphosphinin, Acetylenic ester, Multi-component reactions

INTRODUCTION

Due to the atom economy, convergent character, and simplicity of one-pot procedures, multi-component condensation reactions (MCRs) have an advantageous position among other reactions. The discovery and development of novel MCRs is receiving growing interest from industrial chemistry research groups and represents a new challenge for organic chemists and to the basic understanding of organic chemistry itself [1,2].

Organophosphorus compounds are well known for their biological activity (mainly as insecticides and fungicides) and have increasingly been used in asymmetric organic chemistry, as illustrated by numerous examples in the literature of the application of these compounds in a wide range of chemical reactions [3]. Thus, a large number of methods have appeared describing their syntheses [4].

We have recently reported a convenient route for the synthesis fully substituted *N*-alkyl-2-triphenylphosphoranylidene glutarimides by a novel three-component condensation reaction strategy using isocyanide, dialkyl acetylenedicarboxylate and (ethoxycarbonylmethyl)triphenylphosphonium bromide [5]. The work reported here was undertaken in order to study the possibility of reaction of triphenylphosphine **1**, instead of isocyanide, and an electron-deficient acetylenic ester **2** with ethyl bromoacetate **3** in CH_2Cl_2 at room temperature.

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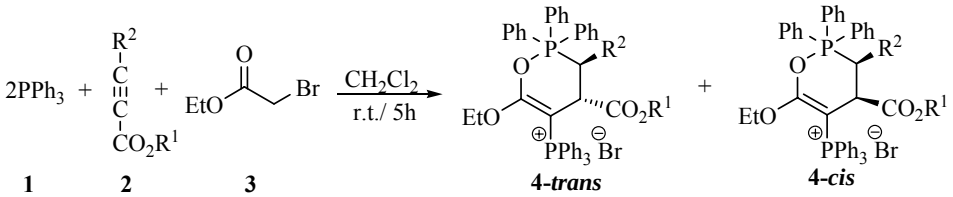
EXPERIMENTAL

Typical Procedure for the Preparation of ((*S*)-3,4-Bis-*tert*-butoxycarbonyl-6-ethoxy-2,2,2-triphenyl-3,4-dihydro-2*H*-2λ^5-[1,2]oxaphosphinin-5-yl)-triphenylphosphonium Bromide (4a)

To a magnetically stirred solution of ethyl bromoacetate (0.17 g, 1 mmol) and triphenylphosphine (0.52 g, 2 mmol) in dichloromethane (10 ml) was added dropwise a solution of di-*tert*-butyl acetylenedicarboxylate (0.26 g, 1 mmol) in dichloromethane (2 ml) at -5 ºC over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 5 h. The solvent was removed under reduced pressure and the product was crystallized from 2:1 ethyl



1 **2** **3**

2,4	R^1	R^2	Yield of **4** (%)
a	^{t}Bu	$CO_2{}^t$Bu	58
b	Et	CO_2Et	60
c	Me	CO_2Me	68
d	Me	H	61

Scheme 1

acetate:hexane mixture and washed with ethyl acetate (3 × 5 ml) and the product **4a** was obtained as white powder (0.53 g, yield 58%); mp 141-143 ºC (dec). IR (KBr): 1721, 1718 (C=O) cm^{-1}. MS, *m/z* (%) = 347 (M^+-((CH$_3$)$_3$CCO$_2$)CH-CH((CH$_3$)$_3$CCO$_2$)PPh$_3$, Br, 15), 262 (60), 183 (55), 152 (10), 108 (50), 77 (20), 57 (40), 41 (100).

4a-*trans* (87%). ^{1}H NMR (300 MHz, CDCl$_3$): δ_H (ppm) 0.73, 0.78 (18H, 2s, 2C(C*H*$_3$)$_3$), 0.78 (3H, t, $^3J_{HH}$ = 6.7 Hz, O-CH$_2$-C*H*$_3$), 2.46-3.66 (3H, m, P-CH-C*H*, O-CH$_2$-C*H*$_3$), 5.82 (1H, pt, $^3J_{HH}$ = $^2J_{PH}$ = 11.5 Hz, P-C*H*-CH), 7.04-7.69 (30H, m, 2PPh$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C (ppm) 13.3 (O-CH$_2$-*C*H$_3$), 27.7, 28.2 (2C(*C*H$_3$)$_3$), 39.2 (dd, $^1J_{PC}$ = 127.7 Hz, $^3J_{PC}$ = 14.4 Hz, $^+$P-C), 43.9 (dd, $^1J_{PC}$ = 38.5 Hz, $^3J_{PC}$ = 4.4 Hz, P-*C*H-CH), 48.5 (dd, $^2J_{PC}$ = 14.9 Hz, $^2J_{PC}$ = 4.2 Hz, P-CH-*C*H), 62.9 (O-*C*H$_2$-CH$_3$), 78.1, 82.8 (2*C*(CH$_3$)$_3$), 120.0 (d, $^1J_{PC}$ = 87.6 Hz, C_{ipso} of P(C$_6$H$_5$)$_3$), 125.8 (d, $^1J_{PC}$ = 93.1 Hz, C_{ipso} of P(C$_6$H$_5$)$_3$), 128.3 (d, $^3J_{PC}$ = 12.2 Hz, C_{meta} of P(C$_6$H$_5$)$_3$), 129.4 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta} of P(C$_6$H$_5$)$_3$), 133.0 (d, $^4J_{PC}$ = 2.0 Hz, C_{para} of P(C$_6$H$_5$)$_3$), 133.2 (C_{para} of P(C$_6$H$_5$)$_3$), 134.0 (d, $^2J_{PC}$ = 3.4 Hz, C_{ortho} of P(C$_6$H$_5$)$_3$), 134.0 (d, $^2J_{PC}$ = 9.4 Hz, C_{ortho} of P(C$_6$H$_5$)$_3$), 168.4 (C=O), 168.82 (d, $^2J_{PC}$ = 12.1 Hz, P-O-C), 172.8 (d, $^2J_{PC}$ = 2.7 Hz, C=O). ^{31}P NMR (121 MHz, CDCl$_3$): δ_P (ppm) 21.7, 22.9 (2P, 2d, $^4J_{PP}$ = 1.6 Hz, 2P(C$_6$H$_5$)$_3$).

4a-*cis* (13%). ^{1}H NMR (300 MHz, CDCl$_3$): δ_H (ppm) 0.81, 1.34 (18H, 2s, 2C(C*H*$_3$)$_3$) 0.96 (3, t, $^3J_{HH}$ = 6.9 Hz, O-CH$_2$-C*H*$_3$), 2.74-3.88 (3H, m, P-CH-C*H*, O-C*H*$_2$-CH$_3$), 5.35 (1H, pt, $^3J_{HH}$ = $^2J_{PH}$ = 11.3 Hz, P-C*H*-CH), 7.04-7.69 (30H, m, 2P(C$_6$H$_5$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C (ppm) 13.8 (O-CH$_2$-*C*H$_3$), 27.6, 29.2 (2C(*C*H$_3$)$_3$), 39.7 (dd, $^1J_{PC}$ = 123.0 Hz, $^3J_{PC}$ = 14.3 Hz, $^+$P-C), 45.9 (dd, $^1J_{PC}$ = 37.0 Hz, $^3J_{PC}$ = 4.5 Hz, P-*C*H-CH), 47.4 (dd, $^2J_{PC}$ = 14.3 Hz, $^2J_{PC}$ = 4.3 Hz, P-CH-*C*H), 63.0 (O-*C*H$_2$-CH$_3$), 78.7, 83.0 (2*C*(CH$_3$)$_3$), 119.9 (d, $^1J_{PC}$ = 83.6 Hz, C_{ipso} of P(C$_6$H$_5$)$_3$), 124.4 (d, $^1J_{PC}$ = 88.7 Hz, C_{ipso} of P(C$_6$H$_5$)$_3$), 128.4 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta} of P(C$_6$H$_5$)$_3$), 128.7 (d, $^3J_{PC}$ = 10.8 Hz, C_{meta} of P(C$_6$H$_5$)$_3$), 132.2 (d, $^4J_{PC}$ = 2.3 Hz, C_{para} of P(C$_6$H$_5$)$_3$), 132.7 (d, $^4J_{PC}$ = 2.2 Hz, C_{para} of P(C$_6$H$_5$)$_3$), 133.8 (d, $^2J_{PC}$ = 9.9 Hz, C_{ortho} of P(C$_6$H$_5$)$_3$), 134.9 (d, $^2J_{PC}$ = 8.6 Hz, C_{ortho} of P(C$_6$H$_5$)$_3$), 167.8 (C=O), 169.6 (d, $^2J_{PC}$ = 14.7 Hz, P-O-C), 173.0 (C=O). ^{31}P NMR (121 MHz, CDCl$_3$): δ_P (ppm) 23.6, 24.4 (2P, 2d, $^4J_{PP}$ = 1.5 Hz, 2P(C$_6$H$_5$)$_3$).

((*S*)-6-Ethoxy-3,4-bis-ethoxycarbonyl-2,2,2-triphenyl-3,4-dihydro-2*H*-2λ^5-[1,2]oxaphosphinin-5-yl)-triphenyl-phosphonium Bromide (4b)

White powder (0.52 g, yield 60%); mp 169-171 ºC (dec). IR (KBr): 1729, 1725 (C=O) cm^{-1}. MS, *m/z* (%) = 348 (M^+-(C$_2$H$_5$CO$_2$)CH-CH(C$_2$H$_5$CO$_2$)PPh$_3$, Br, 10), 262 (55), 183 (50), 152 (10), 108 (60), 77 (40), 44 (100).

4b-*trans* (96%). ^{1}H NMR (300 MHz, CDCl$_3$): δ_H (ppm) 0.35 (3H, t, $^3J_{HH}$ = 6.9 Hz, O-CH$_2$-C*H*$_3$), 0.68 (3H, t, $^3J_{HH}$ = 6.9 Hz, O-CH$_2$-C*H*$_3$), 0.89 (3H, t, $^3J_{HH}$ = 6.7 Hz, O-CH$_2$-C*H*$_3$), 2.88-3.81 (7H, m, P-CH-C*H*, 3O-C*H*$_2$-CH$_3$), 6.05 (1H, pt, $^3J_{HH}$ = $^2J_{PH}$ = 11.4 Hz, P-C*H*-CH), 7.19-7.76 (30H, m, 2P(C$_6$H$_5$)$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ_C (ppm) 13.4, 13.8, 13.8 (3O-

CH_2-*C*H_3), 39.6 (dd, $^1J_{PC}$ = 125.7 Hz, $^3J_{PC}$ = 14.9 Hz, $^+$P-C), 43.4 (dd, $^1J_{PC}$ = 37.9 Hz, $^3J_{PC}$ = 4.8 Hz, P-*C*H-CH), 47.0 (dd, $^2J_{PC}$ = 14.6 Hz, $^2J_{PC}$ = 4.0 Hz, P-CH-*C*H), 58.4, 62.0, 63.2 (3O-*C*H_2-CH_3), 120.0 (d, $^1J_{PC}$ = 87.1 Hz, C_{ipso} of P(C_6H_5)$_3$), 125.7 (d, $^1J_{PC}$ = 95.4 Hz, C_{ipso} of P(C_6H_5)$_3$), 128.7 (d, $^3J_{PC}$ = 12.6 Hz, C_{meta} of P(C_6H_5)$_3$), 129.6 (d, $^3J_{PC}$ = 12.9 Hz, C_{meta} of P(C_6H_5)$_3$), 132.8 (C_{para} of P(C_6H_5)$_3$), 133.4 (C_{para} of P(C_6H_5)$_3$), 134.1 (d, $^2J_{PC}$ = 9.7 Hz, C_{ortho} of P(C_6H_5)$_3$), 134.5 (d, $^2J_{PC}$ = 2.3 Hz, C_{ortho} of P(C_6H_5)$_3$), 168.1 (C=O), 169.7 (d, $^2J_{PC}$ = 12.6 Hz, P-O-C), 172.8 (d, $^2J_{PC}$ = 2.8 Hz, C=O). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 22.7, 23.4 (2P, 2d, $^4J_{PP}$ = 2.3 Hz, 2P(C_6H_5)$_3$).

4b-*cis* (4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 0.77 (3H, t, $^3J_{HH}$ = 6.9 Hz, O-CH_2-C*H*$_3$), 1.14 (3H, t, $^3J_{HH}$ = 6.9 Hz, O-CH_2-C*H*$_3$), 1.32 (3H, t, $^3J_{HH}$ = 6.7 Hz, O-CH_2-C*H*$_3$), 2.88-4.16 (7H, m, P-CH-C*H*, 3O-C*H*$_2$-CH_3), 5.59 (1H, pt, $^3J_{HH}$ = $^2J_{PH}$ = 11.3 Hz, P-C*H*-CH), 7.19-7.76 (30H, m, 2P(C_6H_5)$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 14.0, 14.2, 15.5 (3O-CH_2-*C*H_3), 40.3 (dd, $^1J_{PC}$ = 126.7 Hz, $^3J_{PC}$ = 16.0 Hz, $^+$P-C), 44.6 (dd, $^1J_{PC}$ = 38.2 Hz, $^3J_{PC}$ = 4.6 Hz, P-*C*H-CH), 46.3 (dd, $^2J_{PC}$ = 14.3 Hz, $^2J_{PC}$ = 3.6 Hz, P-CH-*C*H), 59.0, 60.4, 63.4 (3O-*C*H_2-CH_3), 119.6 (d, $^1J_{PC}$ = 86.1 Hz, C_{ipso} of P(C_6H_5)$_3$), 125.8 (d, $^1J_{PC}$ = 90.5 Hz, C_{ipso} of P(C_6H_5)$_3$), 129.0 (d, $^3J_{PC}$ = 12.6 Hz, C_{meta} of P(C_6H_5)$_3$), 130.3 (d, $^3J_{PC}$ = 13.8 Hz, C_{meta} of P(C_6H_5)$_3$), 132.4 (C_{para} of P(C_6H_5)$_3$), 133.0 (C_{para} of P(C_6H_5)$_3$), 133.7 (d, $^2J_{PC}$ = 9.2 Hz, C_{ortho} of P(C_6H_5)$_3$), 134.7 (C_{ortho} of P(C_6H_5)$_3$), 167.7 (C=O), 171.8 (d, $^2J_{PC}$ = 12.5 Hz, P-O-C), 173.1 (d, $^2J_{PC}$ = 3.4 Hz, C=O). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 23.3, 23.7 (2P, 2d, $^4J_{PP}$ = 2.5 Hz, 2P(C_6H_5)$_3$).

((*S*)-6-Ethoxy-3,4-bis-methoxycarbonyl-2,2,2-triphenyl-3,4-dihydro-2*H*-2λ^5-[1,2]oxaphosphinin-5-yl)-triphenyl-phosphonium Bromide (4c)

White powder (0.57 g, yield 68%); m.p.: 171-173 ºC (dec). IR (KBr): 1729, 1726 (C=O) cm^{-1}. MS, *m/z* (%) = 347 (M^+-((CH_3CO_2)CH-CH(CH_3CO_2)PPh_3, Br, 20), 333 (30), 303 (60), 262 (65), 183 (100), 77 (40), 44 (100).

4c-*trans* (61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 0.34 (3H, t, $^3J_{HH}$ = 6.4 Hz, O-CH_2-C*H*$_3$), 3.13, 3.16 (6H, 2s, 2O-CH_3), 3.46-3.76 (3H, m, P-CH-C*H*, O-C*H*$_2$-CH_3), 6.13 (1H, pt, $^3J_{HH}$ = $^2J_{PH}$ = 11.2 Hz, P-C*H*-CH), 7.19-7.65 (30H, m, 2PPh_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 11.8 (O-CH_2-*C*H_3), 38.4 (dd, $^1J_{PC}$ = 127.4 Hz, $^3J_{PC}$ = 15.4 Hz, $^+$P-C), 42.1 (dd, $^1J_{PC}$ = 37.8 Hz, $^3J_{PC}$ = 5.2 Hz, P-*C*H-CH), 45.1 (dd, $^2J_{PC}$ = 15.6 Hz, $^2J_{PC}$ = 3.9 Hz, P-CH-*C*H), 51.1, 52.0 (2O-CH_3), 61.8 (O-*C*H_2-CH_3), 117.5-132.9 (8C, m, 2P(C_6H_5)$_3$), 166.6 (C=O), 168.3 (d, $^2J_{PC}$ = 13.12 Hz, P-O-C), 171.7 (d, $^2J_{PC}$ = 2.5 Hz, C=O). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 23.5, 23.5 (2P, 2d, $^4J_{PP}$ = 1.5 Hz, 2P(C_6H_5)$_3$).

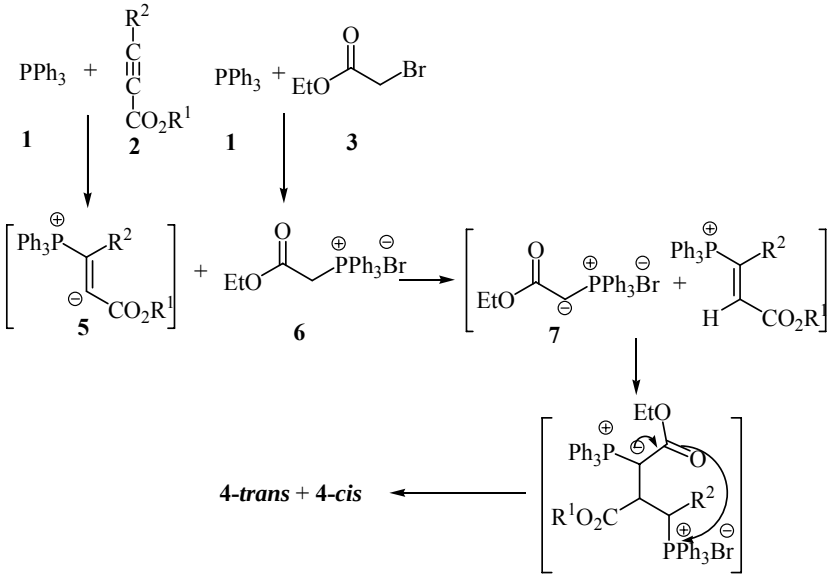
4c-*cis* (39%). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 0.9 (3H, t, $^3J_{HH}$ = 6.9 Hz, O-CH_2-C*H*$_3$), 2.93, 3.15 (6H, 2s, 2O-CH_3), 4.09-4.45 (3H, m, P-CH-C*H*, O-C*H*$_2$-CH_3), 5.66 (1H, dd, $^3J_{HH}$ = $^2J_{PH}$ = 11.1 Hz, P-C*H*-CH), 7.19-7.65 (30H, m, 2PPh_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 12.0 (O-CH_2-*C*H_3), 38.9 (dd, $^1J_{PC}$ = 120.2 Hz, $^3J_{PC}$ = 17.6 Hz, $^+$P-C), 41.9 (dd, $^1J_{PC}$ = 37.9 Hz, $^3J_{PC}$ = 4.9 Hz, P-*C*H-CH), 45.2 (dd, $^2J_{PC}$ = 15.4 Hz, $^2J_{PC}$ = 2.64 Hz, P-CH-*C*H), 51.0, 51.9 (2O-CH_3), 56.76 (O-*C*H_2-CH_3), 117.5-132.9 (8C, m, 2P(C_6H_5)$_3$), 166.5 (C=O), 166.7 (d, $^2J_{PC}$ = 15.0 Hz, P-O-C), 171.6 (d, $^2J_{PC}$ = 2.6 Hz, C=O). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 22.7, 22.9 (2P, 2d, $^4J_{PP}$ = 2.1 Hz, 2P(C_6H_5)$_3$).

((*S*)-6-Ethoxy-4-methoxycarbonyl-2,2,2-triphenyl-3,4-dihydro-2*H*-2λ^5-[1,2]oxaphosphinin-5-yl)-triphenyl-phosphonium Bromide (4d)

White powder (0.47 g, yield 61%); m.p.: 136-138 ºC (dec). IR (KBr): 1734, 1729 (C=O) 1105 cm^{-1}. MS, *m/z* (%) = 347 (M^+-$CH_3CO_2CHCH_2PPh_3$, Br, 15), 262 (58), 183 (55), 152 (12), 108 (65), 77 (30), 44 (100). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 0.46 (3H, t, $^3J_{HH}$ = 7.0 Hz, O-CH_2-C*H*$_3$), 2.68 (1H, m, P-C*H*$_2$-CH), 3.09 (1H, m, P-C*H*$_2$-CH), 3.28 (3H, s, O-CH_3), 3.73 (2H, q, $^3J_{HH}$ = 7.0 Hz, O-C*H*$_2$-CH_3), 4.69-4.82 (H, m, P-CH_2-C*H*), 7.38-7.81 (30H, m, 2PPh_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 13.8 (O-CH_2-*C*H_3), 27.0 (dd, $^1J_{PC}$ = 43.4 Hz, $^3J_{PC}$ = 4.3 Hz, P-*C*H_2-CH), 40.0 (dd, $^2J_{PC}$ = 14.6 Hz, $^2J_{PC}$ = 3.8 Hz, P-CH_2-*C*H), 42.1 (dd, $^1J_{PC}$ = 125.8 Hz, $^3J_{PC}$ = 14.0 Hz, $^+$P-C), 52.4 (O-CH_3), 58.09 (O-*C*H_2-CH_3), 119.0 (d, $^1J_{PC}$ = 86.4 Hz, C_{ipso} of P(C_6H_5)$_3$), 125.9 (d, $^1J_{PC}$ = 92.1 Hz, C_{ipso} of P(C_6H_5)$_3$), 129.1 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta} of P(C_6H_5)$_3$), 133.3 (d, $^3J_{PC}$ = 12.5 Hz, C_{meta} of P(C_6H_5)$_3$), 132.7 (d, $^4J_{PC}$ = 2.4 Hz, C_{para} of P(C_6H_5)$_3$), 133.4 (d, $^2J_{PC}$ = 9.1 Hz, C_{ortho} of P(C_6H_5)$_3$), 133.5 (d, $^2J_{PC}$ = 9.0 Hz, C_{ortho} of P(C_6H_5)$_3$), 135.0 (d, $^4J_{PC}$ = 2.7 Hz, C_{para} of P(C_6H_5)$_3$), 169.6 (d, $^2J_{PC}$ = 12.6 Hz, P-O-C), 173.8 (d, $^3J_{PC}$ = 4.9 Hz, C=O). ^{31}P NMR (121 MHz, $CDCl_3$): δ_P (ppm) 22.0, 22.7 (2P, 2s, 2P(C_6H_5)$_3$).

RESULTS AND DISCUSSION

The reaction of triphenylphosphine and an electron-deficient acetylenic ester with ethyl bromoacetate in CH_2Cl_2



Scheme 2

proceeded at room temperature and finished within 5 h (Scheme 1). The ^{1}H NMR spectra of crude products indicated this pseudo four-component reaction produced 2λ^5-[1,2]oxaphosphinin as **4**-*trans* and **4**-*cis* isomer in about 61-100% to 0-39% mole ratio, respectively.

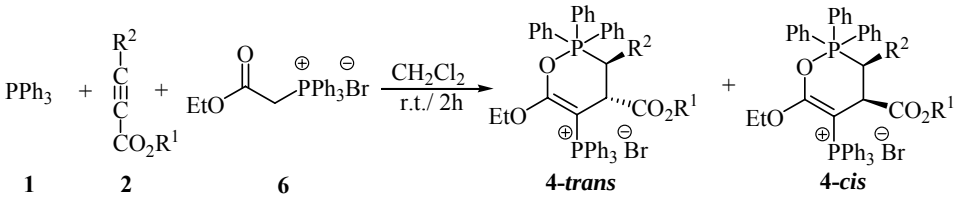
All compounds **4a-d** are stable solid powders whose structures are fully supported by ^{1}H, ^{13}C and ^{31}P NMR and IR spectral data. The ^{1}H NMR spectrum of **4a** consisted of four sets of sharp lines for the *tert*-butyl groups (δ = 0.73, 0.78 ppm for **4**-*trans* and δ = 0.81, 1.34 ppm for **4**-*cis*), two sets of triplet for the methyl groups (OCH_2CH_3, δ = 0.78 ppm, $^3J_{HH}$ = 6.7 Hz for **4**-*trans* and δ = 0.96 ppm, $^3J_{HH}$ = 6.9 Hz for **4**-*cis*), two sets of multiplet for the P-CH-C*H* and methylene group of OCH_2CH_3 which overlap in each isomer (δ = 2.46-3.66 ppm for **4**-*trans* and δ = 2.74-3.88 ppm for **4**-*cis*), two sets of doublet of doublet for the P-C*H*-CH (δ = 5.35 ppm, $^3J_{HH}$ = $^2J_{PH}$ = 11.3 Hz for **4**-*trans* and δ = 5.82 ppm, $^3J_{HH}$ = $^2J_{PH}$ = 11.5 Hz for **4**-*cis*) and the phenyl moieties gave rise to multiplets in the aromatic region of the spectrum (δ = 7.04-7.69 ppm for **4**-*trans* and **4**-*cis*).

The ^{1}H decoupled ^{13}C NMR spectrum of **4a** showed two sets of 20 distinct resonances for **4**-*trans* and **4**-*cis* (^{31}P coupled), the partial assignment of which is given in the experimental section. The ^{31}P NMR spectrum of **4a** exhibited four sets of doublet at (δ = 21.7, 23.0 ppm, $^4J_{PP}$ = 1.6 Hz for **4**-*trans* and δ = 23. 6, 24.4 ppm, $^4J_{PP}$ = 1.5 Hz for **4**-*cis*).

To explore the scope and limitations of this reaction, we extended the procedure to various acetylenic esters in the presence of triphenylphosphine and ethyl bromoacetate. Based on ^{1}H NMR and ^{13}C NMR spectra of the crude reactions, we found that the **4**-*trans* and **4**-*cis* isomers were produced with dimethyl acetylenedicarboxylate, diethyl acetylene-dicarboxylate and di-*tert*-butyl acetylenedicarboxylate, however, when methyl propiolate (**2d**) was used only one isomer was obtained.

On the basis of well established chemistry of trivalent phosphorus nucleophiles [6-9,3], it is reasonable to assume that phosphorus ylide **5** and compound **6** result from the initial addition of triphenylphosphine to the acetylenic ester [9] and ethyl bromoacetate, respectively, and subsequent protonation of the highly reactive 1:1 adduct **5** by the CH-acid **6**. Then, the positively charged ion is attacked by the enolate anion of the CH-acid **7** and followed by intramolecular nucleophilic attack of oxygen to phosphorus under the reaction conditions to produce **4** (Scheme 2).

To check whether the proposed mechanism is reasonable, we have carried out the reaction under three-component condensation conditions as follows. First, compound **6** is



2,4	R^1	R^2	Yield of **4** (%)
a	^{t}Bu	CO2^{t}Bu	91
b	Et	CO_2Et	93
c	Me	CO_2Me	95
d	Me	H	90

Scheme 3

prepared by the reaction of compounds **1** and **3**, and then, the reaction of compound **6** with compounds **1** and **2** is followed. It was found that the reaction proceeds very efficiently and yields are increased to 91-95% relative to pseudo four-component condensation reaction. The aforementioned results have confirmed the proposed mechanism (Scheme 3).

It is important to note that the pseudo four-component condensation reaction with triphenylphosphine can be easily carried out. While, in the previously our report [5], we found that the reaction of isocyanide by the four-component reaction strategy is completely stopped.

In conclusion, we have devised a novel pseudo four-component condensation reaction leading to fully functionalized 2λ^5-[1,2]oxaphosphinin derivatives from simple and readily available precursors under neutral conditions without any activation or modification.

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