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Solvent-free (neat) synthesis of stable phosphorus ylides using alkyl phenylcarbamates

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Efficient synthesis of dimethyl 2-[(alkoxycarbonyl)anilino-3-(1,1,1-triphenyl-λ^5-phosphanylidene) succinate derivatives with good yields is described. The method involves three-component reaction between triphenylphosphine, dimethyl acetylenedicarboxylates and alkyl phenylcarbamate under solvent-free conditions at room temperature.

Keywords: alkyl phenylcarbamate, phosphorus ylides, solvent-free condition, triphenylphosphine.

INTRODUCTION

Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, and compounds with biological and pharmacological activity [1-6]. The prominent role of these compounds is to convert the carbonyl groups to carbon-carbon double bonds [7-8]. Many methods have been reported on the preparation and structural analysis of phosphorus ylides [9-14]. From the large number of methods available, the most important ones involve reaction of a phosphonium salt with a base [15-16]. There are many studies on the reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source such as OH, CH, NH or SH [17-31]. Here we describe an efficient synthetic route for the preparation of stable phosphorus ylides **3** using triphenylphosphine, dimethyl acetylenedicarboxylates **2** and alkyl phenylcarbamate **1** under solvent-free conditions at room temperature (Scheme 1).

EXPERIMENTAL

General

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker FT-500 spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded with a Finnigan Mat TSQ-70 spectrometer. Infrared (IR) spectra were acquired on a Nicolet Magna 550-FT spectrometer. Elemental analyses were carried out with a Perkin-Elmer model 240-C apparatus. The results of the elemental analyses (C, H, N) were within ±0.4 % of the calculated values. Dimethyl acetylenedicarboxylates and triphenyl phosphine were obtained from Fluka and were used without further purification.

General procedure for the preparation of compounds 3a-g

To a magnetically stirred mixture of an alkyl phenylcarbamate **1** (2 mmol) and dimethyl acetylenedicarboxylate **2** (2 mmol) triphenylphosphine (2 mmol) was slowly added, and the reaction mixture was stirred for 4 h at room temperature. After completion of the reaction, as indicated by TLC, the residue was purified by chromatography over silica gel (Merck 230-400 mesh) using an *n*-hexane-AcOEt mixture (2:1) as eluent, to afford the pure adducts.

RESULTS AND DISCUSSION

The reaction between alkyl phenylcarbamate **1,** dimethyl acetylenedicarboxylates **2** and triphenylphosphine proceeded smoothly under solvent-free conditions at room temperature to produce dimethyl 2-[(alkoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate derivatives **3** in 90 – 95 % yield (Scheme 1).

The structures of compounds **3a-g** were determined by elemental analysis, mass, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The ^{1}H, ^{13}C, and ^{31}P NMR spectra revealed that the ylides **3a-g** are mixtures of two isomers. According to the structure of the stable phosphorus ylides determined by X-ray [32-33], the ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and the rotation about the partial double bond in **E**, **Z** geometrical isomers is low on the NMR time scale at ambient temperature (Scheme 2). Conformational

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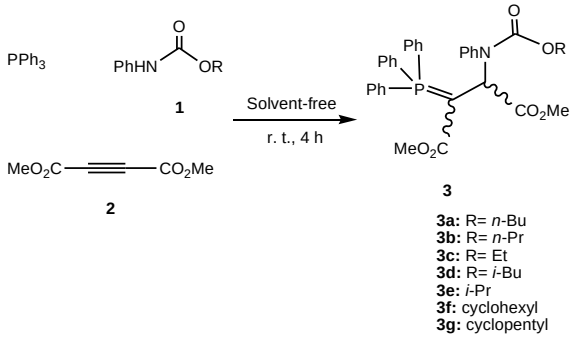
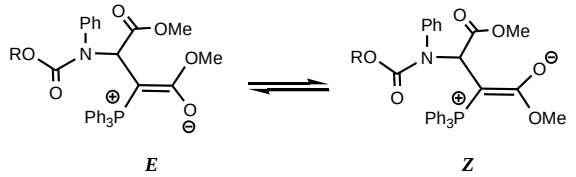
isomers in phosphoranes have been previously established and reported in the literature [34-37].



Scheme 1. Synthesis of compounds **3a-g**.



Scheme 2. Geometrical isomers of 3a-g.

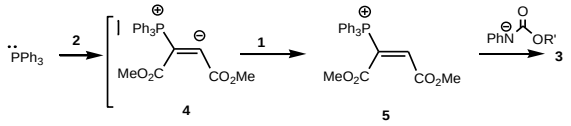
The ^{1}H NMR spectrum of compound **3a** showed two singlets at δ 3.73 and 3.82 ppm for two methoxy groups and 3.82 for the major isomer (Z-isomer), along with a signal for the methine proton at δ 4.96 ppm which appeared as a doublet ($^3J_{PH}$ = 17.8 Hz). This spectrum also exhibited signals at δ 0.80, 1.10-1.14, 1.28-1.32 and 3.86 ppm for the butyl moiety in the major isomer.

The corresponding signals for the minor isomer (E-isomer) were two signals at δ 3.70 and 3.80 ppm for methoxy groups and a doublet at δ 4.83 ppm ($^3J_{PH}$ = 16.8 Hz) for the methine proton. Four signals appeared at δ 0.84, 1.15-1.21, 1.33-1.38 and 4.02 ppm assigned to the butyl moiety in this isomer.

The ^{13}C NMR spectrum of **3a** displayed signals agreeing with the mixture of two geometrical isomers of Z and E. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of **3a**, it helps in the assignment of signals by long range spin–spin couplings with ^{1}H and ^{13}C nuclei. The ^{1}H NMR and ^{13}C NMR spectral data for compounds **5b–g** are consistent with the geometrical isomers.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles, it is reasonable to assume that the phosphorus ylide **3** results from the initial addition of triphenylphosphine to the dimethyl acetylenedicarboxylates and subsequent protonation of the 1:1 adduct by the phenylcarbamate to form **3** (Scheme 3) [38-41].

In conclusion, the reaction between dimethyl acetylenedicarboxylates, phenylcarbamates, and triphenylphosphine provides a simple one-pot synthesis of stable phosphorus ylides of potential synthetic interest.



Scheme 3. Possible mechanism for the formation of compounds **3**.

The present procedure has the following advantages: (i) the reaction is performed under solvent-free conditions, and (ii) the starting material can be used without any activation or modification. The procedure described here provides an acceptable method for the preparation of phosphoranes with variable functionalities.

*Dimethyl-2-[(butoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3a**)*

Yellow oil, yield, 1.13 g (95%). IR (KBr) (υ_{max}/cm^{-1}): 2958 (CH), 1752 (C=O), 1692 (C=O), 1434, 1102, 996 (P-Ph). **NMR data for the major isomer (Z) (60 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.80 (t, 3H, J = 6.8 Hz, $O(CH_2)_3CH_3$), 1.10-1.14 (m, 2H, $O(CH_2)_2CH_2CH_3$), 1.28-1.32 (m, 2H, $OCH_2CH_2CH_2CH_3$), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.86 (t, 2H, J = 6.9 Hz, $OCH_2(CH_2)_2CH_3$), 4.96 (d, 1H, J_{PH} = 17.8 Hz, H-2), 7.23-7.42 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.7 ($O(CH_2)_3CH_3$), 18.8 ($O(CH_2)_2CH_2CH_3$), 29.7 ($OCH_2CH_2CH_2CH_3$), 41.3 (d, $^1J_{PC}$ = 134.0 Hz, C-3), 52.1 (OCH_3), 52.3 (OCH_3), 60.9 (d, $^2J_{PC}$ = 16.0 Hz, C-2), 64.9 ($OCH_2(CH_2)_2CH_3$), 126.4 (d, $^1J_{PC}$ = 98.0 Hz, C-*ipso*), 128.6, 128.7, 128.9 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 10.0 Hz, C-*ortho*), 139.1, 155.4 (C=O), 168.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 173.5 (d, $^3J_{PC}$ = 10.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.76 (PPh_3) ppm. **NMR data for the minor isomer (E) (40 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.84 (t, 3H, J = 7.1 Hz, $O(CH_2)_3CH_3$), 1.15-1.21 (m, 2H, $O(CH_2)_2CH_2CH_3$), 1.33-1.38 (m, 2H, $OCH_2CH_2CH_2CH_3$), 3.70 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.02 (t, 2H, J = 6.8 Hz, $OCH_2(CH_2)_2CH_3$), 4.83 (d, 1H, $^3J_{PH}$ = 16.8 Hz, H-2), 7.49-7.66 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.8 ($O(CH_2)_3CH_3$), 18.9 (m, 2H, $O(CH_2)_2CH_2CH_3$), 30.2 ($OCH_2CH_2CH_2CH_3$), 42.2 (d, $^1J_{PC}$ = 137.2 Hz, C-3), 48.8 (OCH_3), 49.5 (OCH_3), 61.8 (d, $^2J_{PC}$ = 17.0 Hz, C-2), 64.8 ($OCH_2(CH_2)_2CH_3$), 126.7 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.5, 128.6, 129.1 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 10.0 Hz, C-*ortho*), 139.4, 154.0 (C=O), 173.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.1 (d, $^3J_{PC}$ = 9.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.11 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 597 (M^+, 2),

538 (12), 405 (38), 335 (15), 262 (42), 192 (51). Anal. Calcd for $C_{35}H_{36}NO_6P$: C 70.34; H 6.07; N 2.34; found: C 70.36; H 6.05; N 2.37.

*Dimethyl-2-[(propoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3b**)*

Yellow oil, yield: 1.08 g (93%). IR (KBr) (υ_{max}/ cm^{-1}): 2961 (CH), 1754 (C=O), 1695 (C=O), 1432, 1105, 995 (P-Ph). **NMR data for the major isomer (Z) (63 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (t, 3H, *J* = 6.9 Hz, $(OCH_2)_2CH_3$), 1.67 (sixtet, 2H, *J* = 7.0 Hz, $(OCH_2CH_2CH_3)$, 3.68 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.80 (t, *J* = 6.8 Hz, $(OCH_2CH_2CH_3)$, 4.80 (d, $^3J_{PH}$ = 18.0 Hz, H-2), 7.17-7.38 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 11.4 ($(OCH_2)_2CH_3$), 23.0 ($OCH_2CH_2CH_3$), 41.5 (d, $^1J_{PC}$ = 134.5 Hz, C-3), 52.1 (OCH_3), 52.3 (OCH_3), 61.0 (d, $^2J_{PC}$ = 17.2 Hz, C-2), 64.7 ($OCH_2CH_2CH_3$), 126.5 (d, $^1J_{PC}$ = 99.0 Hz, C-*ipso*), 128.5, 128.6, 128.7 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 140.0, 155.3 (C=O), 168.4 (d, $^2J_{PC}$ = 13.2 Hz, C=O), 173.3 (d, $^3J_{PC}$ = 10.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* 24.73 (PPh_3) ppm. **NMR data for the minor isomer (E) (37 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (t, 3H, *J* = 7.0 Hz, $((OCH_2)_2CH_3)$, 1.63 (sixtet, 2H, *J* = 7.1 Hz, $(OCH_2CH_2CH_3)$, 3.70 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 4.10 (t, 2H, *J* = 6.8 Hz, $(OCH_2CH_2CH_3)$, 4.88 (d, 1H, $^3J_{PH}$ = 17.0 Hz, H-2), 7.43-7.61 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 11.0 ($((OCH_2)_2CH_3)$, 23.2 ($OCH_2CH_2CH_3$), 42.1 (d, $^1J_{PC}$ = 136.0 Hz, C-3), 48.7 (OCH_3), 49.5 (OCH_3), 61.6 (d, $^2J_{PC}$ = 16.8 Hz, C-2), 64.6 ($OCH_2CH_2CH_3$), 126.8 (d, $^1J_{PC}$ = 95.0 Hz, C-*ipso*), 128.3, 128.5, 128.6 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 131.8, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 9.8 Hz, C-*ortho*), 139.6, 154.2 (C=O), 173.1 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.0 (d, $^3J_{PC}$ = 9.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* 29.10 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 583 (M^+, 3), 524(15), 405 (38), 321 (17), 262 (41), 178 (54). Anal. Calcd for $C_{34}H_{34}NO_6P$: C 69.97; H 5.87; N 2.40; found: C 69.96; H 5.88; N 2.37.

*Dimethyl-2-[(ethoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3c**)*

Yellow oil, yield: 1.08 g (95%). IR (KBr) (υ_{max}, cm^{-1}): 2955 (CH), 1756 (C=O), 1697 (C=O), 1431, 1108, 997 (P-Ph). **NMR data for the major isomer (Z) (64 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.04 (t, 3H, *J* = 6.9 Hz, OCH_2CH_3), 3.64 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 3.97 (q, 2H, *J* = 6.9 Hz, OCH_2CH_3), 4.87 (d, 1H, $^3J_{PH}$ = 17.8 Hz, H-2), 6.73-7.30 (m, 20H, ArH) ppm. (125 MHz, $CDCl_3$): *δ* 14.6 (OCH_2CH_3), 41.4 (d, $^1J_{PC}$ = 134.0 Hz, C-3), 52.2 (OCH_3), 52.4 (OCH_3), 60.1 (OCH_2CH_3), 61.8 (d, $^2J_{PC}$ = 16.2 Hz, C-2), 126.3 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.6, 128.7, 128.8 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 9.6 Hz, C-*ortho*), 139.4, 154.1 (C=O), 168.6 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 173.6 (d, $^3J_{PC}$ = 14.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* 24.68 (PPh_3) ppm. **NMR data for the minor isomer (E) (36 %):** ^{1}H NMR: (500 MHz, $CDCl_3$): δ 1.15 (t, 3H, *J* = 7.0 Hz, OCH_2CH_3), 3.62 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.85 (t, 2H, *J* = 6.9 Hz, OCH_2CH_3), 4.80 (d, 1H,$^3J_{PH}$ = 16.7 Hz, H-2), 7.35-7.56 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 14.5 (OCH_2CH_3), 42.0 (d, $^1J_{PC}$ = 136.8 Hz, C-3), 48.9 (OCH_3), 49.5 (OCH_3), 60.9 (OCH_2CH_3), 61.0 (d, $^2J_{PC}$ = 16.0 Hz, C-2), 126.6 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.5, 128.6, 128.9 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 131.9, 132.0 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 9.0 Hz, C-*ortho*), 139.3, 155.3 (C=O), 170.6 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 173.8 (d, $^3J_{PC}$ = 13.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* 29.13 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 569 (M^+, 4), 496 (10), 405 (36), 307 (17), 262 (43), 164 (48). Anal. Calcd for $C_{34}H_{34}NO_6P$: C 69.59; H 5.66; N 2.46; found: C 69.60; H 5.63; N 2.42.

*Dimethyl-2-[(isobutoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3d**)*

Yellow oil, yield: 1.07 g (90%). IR (KBr) (υ_{max}/ cm^{-1}): 2958 (CH), 1752 (C=O), 1692 (C=O), 1434, 1102, 996 (P-Ph). **NMR data for the major isomer (Z) (63 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (d, 6H, *J* = 6.9 Hz, $OCH_2CH(CH_3)_2$), 1.83 (heptet, 1H, *J* = 7.0 Hz, $OCH_2CH(CH_3)_2$), 3.67 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.79 (d, 2H, *J* = 6.8 Hz, $OCH_2CH(CH_3)_2$), 4.96 (d, 1H, $^3J_{PH}$ = 18.0 Hz, H-2), 6.80-7.43 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 18.9 ($OCH_2CH(CH_3)_2$), 19.1 ($OCH_2CH(CH_3)_2$), 29.6 ($OCH_2CH(CH_3)_2$), 41.3 (d, $^1J_{PC}$ = 134.1 Hz, C-3), 52.1 (OCH_3), 52.3 (OCH_3), 60.9 (d, $^2J_{PC}$ = 14.6 Hz, C-2), 71.1 ($OCH_2CH(CH_3)_2$), 126.7 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.6, 128.7, 128.8 (d, $^3J_{PC}$ = 7.8 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 9.7 Hz, C-*ortho*), 138.9, 154.1 (C=O), 168.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 170.1 (d, $^3J_{PC}$ = 17.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* 24.73 (PPh_3) ppm. **NMR data for the minor isomer (E) (37 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (d, 6H, *J* = 6.9 Hz, $OCH_2CH(CH_3)_2$), 1.60 (heptet, 1H, *J* = 7.0 Hz, $OCH_2CH(CH_3)_2$), 3.66 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.78 (d, 2H, *J* = 6.8 Hz, $OCH_2CH(CH_3)_2$), 4.80 (d, 1H, $^3J_{PH}$ = 16.8 Hz, C-2), 7.45-7.63 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 18.8 ($OCH_2CH(CH_3)_2$), 19.0 ($OCH_2CH(CH_3)_2$), 30.8 ($OCH_2CH(CH_3)_2$), 42.2 (d,

$^1J_{PC}$ = 136.5 Hz, C-3), 48.8 (OCH_3), 49.5 (OCH_3), 61.8 (d, $^2J_{PC}$ = 13.0 Hz, C-2), 71.2 ($OCH_2CH(CH_3)_2$), 126.4 (d, $^1J_{PC}$ = 90.0 Hz, C-*ipso*), 128.5, 128.6, 128.7 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 131.9, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 9.8 Hz, C-*ortho*), 139.1, 154.3 (C=O), 173.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.1 (d, $^3J_{PC}$ = 16.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.09 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 597 (M^+, 3), 538 (13), 405 (43), 335 (21), 262 (43), 192 (55). Anal. Calcd for $C_{35}H_{36}NO_6P$: C 70.34; H 6.07; N 2.34; found: C 70.36; H 6.05; N 2.37.

*Dimethyl-2-[(isopropoxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3e**)*

Yellow oil, yield: 1.10 g (95%). IR (KBr) (υ_{max}/ cm^{-1}): 2960 (CH), 1753 (C=O), 1695 (C=O), 1435, 1103, 994 (P-Ph). **NMR data for the major isomer (Z) (65 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (d, 6H, *J* = 6.9 Hz, $OCH(CH_3)_2$), 3.72 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.84 (heptet, *J* = 6.8 Hz, $OCH(CH_3)_2$), 4.82 (d, $^3J_{PH}$ = 17.9 Hz, H-2), 7.13-7.35 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.8 ($OCH(CH_3)_2$), 41.5 (d, $^1J_{PC}$ = 134.0 Hz, C-3), 52.2 (OCH_3), 52.4 (OCH_3), 61.2 (d, $^2J_{PC}$ = 17.2 Hz, C-2), 64.6 ($OCH(CH_3)_2$), 126.5 (d, $^1J_{PC}$ = 99.0 Hz, C-*ipso*), 128.4, 128.6, 128.7 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 9.5 Hz, C-*ortho*), 140.0, 155.3 (C=O), 168.4 (d, $^2J_{PC}$ = 13.2 Hz, C=O), 173.3 (d, $^3J_{PC}$ = 10.0 Hz, C=O) ppm. ^{31}P NMR: δ 24.75 (PPh_3) ppm. **NMR data for the minor isomer (E) (35 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (d, 6H, *J* = 6.8 Hz, $OCH(CH_3)_2$), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.81 (heptet, 1H, *J* = 6.8 Hz, $OCH(CH_3)_2$), 4.78 (d, 1H, $^3J_{PH}$ = 16.9 Hz, H-2), 7.37-7.56 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.6 ($OCH(CH_3)_2$), 42.2 (d, $^1J_{PC}$ = 136.2 Hz, C-3), 48.8 (OCH_3), 49.4 (OCH_3), 61.8 (d, $^2J_{PC}$= 17.2 Hz, C-2), 64.8 ($OCH(CH_3)_2$), 126.8 (d, $^1J_{PC}$ = 95.0 Hz, C-*ipso*), 128.3, 128.5, 128.6 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 131.9, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 9.8 Hz, C-*ortho*), 139.6, 154.2 (C=O), 173.0 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.1 (d, $^3J_{PC}$ = 9.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.11 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 583 (M^+, 3), 524(13), 405 (39), 321 (20), 262 (43), 178 (58). Anal. Calcd for $C_{34}H_{34}NO_6P$: C 69.97; H 5.87; N 2.40; found: C 69.95; H 5.85; N 2.41.

*Dimethyl-2-[(cyclohexyloxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3f**)*

Yellow oil, yield, 1.14 g (92%). IR (KBr) (υ_{max}/ cm^{-1}): 2958 (CH), 1752 (C=O), 1691 (C=O), 1434, 1105, 996 (P-Ph). **NMR data for the major isomer (Z) (64 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60-1.64 (m, 2H, CH_2), 1.71-1.75 (m, 4H, $2CH_2$), 1.90-1.96 (m, 4H, $2CH_2$), 3.74 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.21 (m, 1H, OCH), 4.93 (d, 1H, $^3J_{PH}$ = 18.0 Hz, H-2), 7.21-7.40 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.4 ($2CH_2$), 25.4 (CH_2), 32.0 ($2CH_2$), 41.2 (d, $^1J_{PC}$ = 134.5 Hz, C-3), 52.2 (OCH_3), 52.4 (OCH_3), 60.9 (d, $^2J_{PC}$ = 16.5, C-2), 64.8 (OCH), 126.4 (d, $^1J_{PC}$ = 98.0 Hz, C-*ipso*), 128.6, 128.7, 128.9 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 10.0 Hz, C-*ortho*), 139.1, 155.4 (C=O), 168.5 (d, $^2J_{PC}$ = 13.0, C=O), 173.5 (d, $^3J_{PC}$ = 10.0, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.77 (PPh_3) ppm. **NMR data for the minor isomer (E) (36 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56-1.59 (m, 2H, CH_2), 1.69-1.73 (m, 4H, $2CH_2$), 1.82-1.90 (m, 4H, $2CH_2$), 3.72 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.23 (m, 1H, OCH), 4.90 (d, 1H, $^3J_{PH}$ = 17.0 Hz, H-2), 7.42-7.53 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2 ($2CH_2$), 25.5 (CH_2), 32.2 ($2CH_2$), 42.1 (d, $^1J_{PC}$ = 136.1 Hz, C-3), 48.7 (OCH_3), 49.6 (OCH_3), 61.3 (d, $^2J_{PC}$ = 16.0 Hz, C-2), 65.2 (OCH), 126.7 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.5, 128.6, 129.1 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 132.0, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 10.0 Hz, C-*ortho*), 139.4, 154.0 (C=O), 173.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.1 (d, $^3J_{PC}$ = 9.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.12 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 623 (4) [M]+, 496 (11), 405 (41), 361 (18), 262 (35), 218 (47). Anal. Calcd for $C_{37}H_{38}NO_6P$: C 71.25; H 6.14; N 2.25; found: C 71.20; H 6.12; N 2.27.

*Dimethyl-2-[(cyclopentyloxycarbonyl)anilino]-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinate (**3g**)*

Yellow oil, yield, 1.14 g (92%). IR (KBr) (υ_{max}/ cm^{-1}): 2953 (CH), 1754 (C=O), 1695 (C=O), 1432, 1102, 998 (P-Ph). **NMR data for the major isomer (Z) (64 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.46-1.56 (m, 4H, $2CH_2$), 1.63-1.76 (m, 4H, $2CH_2$), 3.76 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.19 (m, 1H, OCH), 4.81 (d, 1H, $^3J_{PH}$ = 18.0 Hz, H-2), 6.91-7.42 (m, 20H, ArH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.4 ($2CH_2$), 33.6 ($2CH_2$), 41.1 (d, $^1J_{PC}$ = 134.0 Hz, C-3), 52.1 (OCH_3), 52.3 (OCH_3), 61.1 (d, $^2J_{PC}$ = 17.0 Hz, C-2), 64.9 (OCH), 126.7 (d, $^1J_{PC}$ = 92.0 Hz, C-*ipso*), 128.6, 128.7, 128.8 (d, $^3J_{PC}$ = 7.8 Hz, C-*meta*), 132.0, 132.2 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.7 (d, $^2J_{PC}$ = 9.7 Hz, C-*ortho*), 138.9, 154.1 (C=O), 168.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 170.1 (d, $^3J_{PC}$ = 17.0, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.76 (PPh_3) ppm. **NMR data for the minor isomer (E) (36 %):** ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.57-1.68 (m, 4H, $2CH_2$), 1.77-1.89 (m, 4H, $2CH_2$), 3.74 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 4.17 (m, 1H, $2CH_2$), 4.78 (d, 1H, $^3J_{PH}$ = 17.0 Hz, H-

2), 7.42-7.58 (m, 20H, ArH) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 24.5 ($2CH_2$), 33.8 ($2CH_2$), 42.0 (d, $^1J_{PC}$ = 136.2 Hz, C-3), 48.8 (OCH_3), 49.6 (OCH_3), 61.9 (d, $^2J_{PC}$ = 17.0 Hz, C-2), 64.5 (OCH), 126.4 (d, $^1J_{PC}$ = 90.0 Hz, C-*ipso*), 128.5, 128.6, 128.7 (d, $^3J_{PC}$ = 8.0 Hz, C-*meta*), 131.9, 132.1 (d, $^4J_{PC}$ = 2.0 Hz, C-*para*), 133.5 (d, $^2J_{PC}$ = 9.8 Hz, C-*ortho*), 139.1, 154.3 (C=O), 173.5 (d, $^2J_{PC}$ = 13.0 Hz, C=O), 174.1 (d, $^3J_{PC}$ = 16.0 Hz, C=O) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.20 (PPh_3) ppm. MS (EI, 70 eV) *m*/*z* (%): 609 (M^+, 2), 96 (14), 405 (33), 347 (18), 262 (37), 204 (45). Anal. Calcd for $C_{36}H_{36}NO_6P$: C 70.92; H 5.95; N 2.30; found: C 70.90; H 5.097; N 2.27.

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СИНТЕЗ НА СТАБИЛНИ ФОСФОРНИ ИЛИДИ С АЛКИЛ-ФЕНИЛКАРБАМАТИ БЕЗ РАЗТВОРИТЕЛ

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(Резюме)

Описана е ефикасна синтеза на производни на диметил 2-[(алкоксикарбонил)анилино-3-(1,1,1-трифенил-λ^5-фосфанилиден) сукцинат с добър добив. Методът включва три-компонентна реакция между трифенилфосфин, диметил-ацетилен-дикарбоксилати и алкил-фенилкарбамати без разтворител и при стайна температура.