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Diastereoselective Synthesis of Stable Phosphorus Yields by a Three-Component Reaction between Ph_3P and Acetylenic Esters in the Presence of Hydrazine Derivatives

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Abstract

In this work, stable crystalline phosphorus yields are obtained in good yields from the 1:1:1 addition reactions between hydrazine derivatives and dialkyl acetylenedicarboxylates in the presence of triphenylphosphine at room temperature in dichloromethane. This synthetic method has merits of high yields, mild reaction conditions, and simple experimental and work-up conditions. The obtained yields exist in solution as a mixture of two geometric isomers. This is because of the restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the yields moiety with the adjacent carbonyl group.

***Keywords*:** *Triphenylphosphine, Acetylenic esters, 4-phenylthiosemicarbazide, Phosphorus yields, 2,4-dinitrophenylhydrazine.*

Introduction

Organophosphorus compounds, i.e. those have a carbon atom directly bound to a phosphorus atom, are synthetic targets of interest, at least because of their value for a variety of industrial, biological, and chemical synthetic applications. The development of the modern chemistry of naturally and physiologically active compounds would have been impossible without the phosphorus yields. These compounds have attained great significance as widely used reagents for linking synthetic building blocks with the formation of carbon-carbon double bonds, and this has excited much

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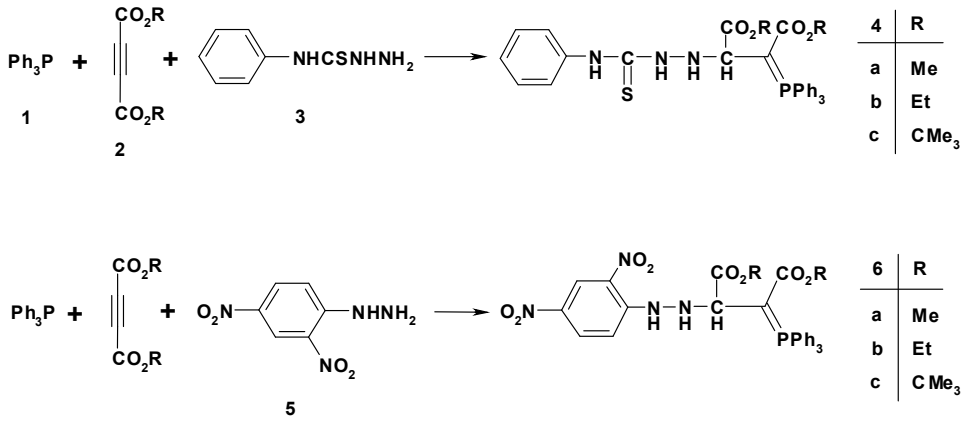
interest in the study of synthesis, structure and properties of phosphorus yields. The stabilized phosphorus yields are able to take part in the normal intramolecular Wittig reactions but they are not generally able to participate in the normal intermolecular Wittig reactions. Several methods have been developed for preparation of phosphorus yields. These yields are most frequently prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are usually made from the reaction of a phosphine with an alkyl halide [1-4]. They are also obtained by the Michael addition of phosphorus nucleophiles to activated olefins [5].

There are many studies on the reaction between trivalent phosphorus nucleophiles and α,β-unsaturated carbonyl compounds in the presence of a proton source [6-13]. We describe herein the synthesis of stabilized phosphorus yields which are prepared by the one-pot and convenient reactions of dialkyl acetylenedicarboxylates 2 with triphenylphosphine as a trivalent phosphorus nucleophile in the presence of 4-phenylthiosemicarbazide and 2,4-dinitrophenylhydrazine as two different proton sources (Scheme 1).



Scheme 1. Reaction equations for formation of the yields **4a-4c** and **6a-6c**.

Experimental

General

Compounds **1-3** and **5** were obtained from Fluka and were used without further purification. The following instruments were used: m.p., Electrothermal-9100 apparatus; IR spectra, Shimadzu IR-460 spectrometer; ^{1}H- and ^{13}C-NMR spectra, Bruker DRX-300 AVANCE instrument; in $CDCl_3$ at 300 MHz and 75 MHz, respectively, δ 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 mass and elemental analyses data were in agreement with the proposed structures.

General procedure for the preparation of

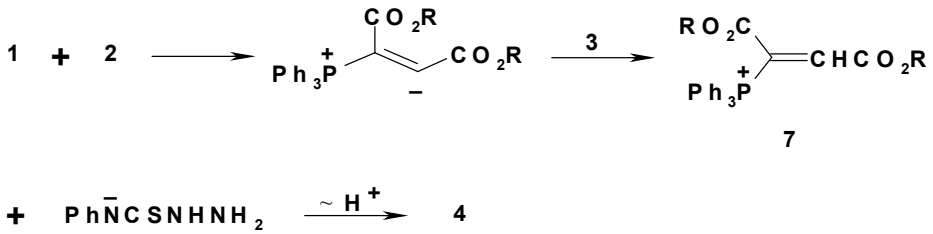
*compounds **4** and **6***

To a magnetically stirred solution of 0.52 g of triphenylphosphine (2 mmol) and **3** (or **5**) (2 mmol) in 10 mL of dry CH_2Cl_2 was added dropwise a solution of a dialkyl acetylenedicarboxylate (2 mmol) in dry CH_2Cl_2 (5 mL) at 0 °C for 10 min. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h. The solvent was removed under reduced pressure, and the residue was recrystallized from Et_2O to afford the pure products.

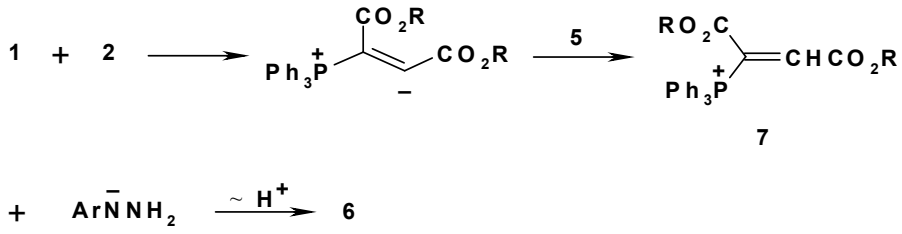
Results and Discussion

The reaction of 4-phenylthiosemicarbazide or 2,4-dinitrophenylhydrazine with the dialkyl acetylenedicarboxylates **2** in the presence of triphenylphosphine proceeded at room temperature in dichloromethane, and was completed within three hours. The structures of yields **4a-4c** and **6a-6c** were deduced from their elemental analyses and IR, ^{1}H-NMR, and ^{13}C-NMR spectra.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles [14-15], it is reasonable to assume that the phosphorus yields **4** and **6** are resulted from the initial addition of triphenylphosphine to acetylenic ester and subsequent protonation of the 1:1 adduct followed by attack of the anion of NH-acid (from NH_2) to the vinylphosphonium cation **7** and then proton shift (Schemes 2 and 3).

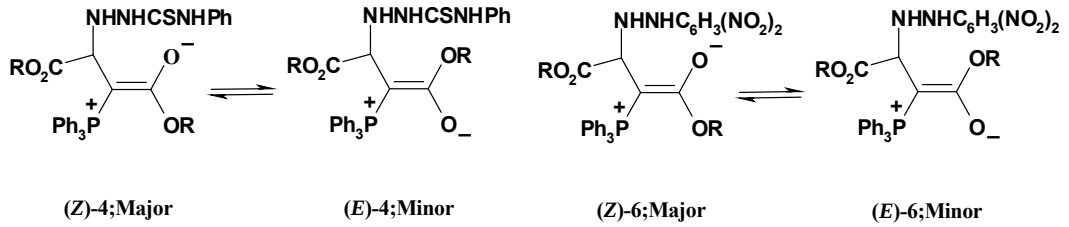


Scheme 2. Reaction details for formation of the yields **4a-4c**.



Scheme 3. Reaction details for formation of the yields **6a-6c**.

^{1}H-NMR and ^{13}C-NMR spectra of the yields **4a-4c** and **6a-6c** are in agreement with the presence of two diastereomers. The yield moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in the (*Z*)-**4** and (*E*)-**4** or (*Z*)-**6** and (*E*)-**6** geometrical isomers is slow on the NMR time scale at ambient temperature [16]. The assignment of **Z**-configuration for the major geometrical isomers of **4** and **6** is based on the ^{1}H-NMR chemical shift of OR moiety. It is expected to be shielded as a result of the anisotropic effect of the phenyl group of phosphine moiety (Scheme 4).



Scheme 4. Configurations of the major and minor geometrical isomers of **4** and **6**.

Selected ^{1}H and ^{13}C chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **4a-4c** and **6a-6c** are shown in Tables 1 and 2.

Table 1. Selected ^{1}H and ^{13}C chemical shifts (δ in ppm) and coupling constants (*J* in Hz) in the major (M) and minor (m) geometrical isomers of compounds 4a-4c.

Compound	Isomer (%)	^{1}H-NMR			^{13}C-NMR
		H-2 ($^3J_{HP}$, $^3J_{HH}$)	CO_2R	OR	C-2 ($^2J_{CP}$)
4a	M (64)	3.24 (15.3, 9.0)	3.79	3.17	63.1 (14.8)
	m (36)	3.49 (13.3, 6.3)	3.77	3.59	62.4 (15.1)
4b	M (67)	3.21 (16.1, 9.1)	4.10–4.22[a]	3.67–3.81[a]	62.9 (14.9)
	m (33)	3.21 (16.1, 9.1)	4.23–4.35[a]	3.93–4.12[a]	61.9 (15.1)
4c	M (76)	3.03 (15.9, 8.5)	1.54	0.95	63.3 (15.5)
	m (24)	2.92 (17.3, 10.1)	1.51	1.46	62.2 (16.7)

[a] *The methylene group of OR moiety*

Table 2. Selected ^{1}H and ^{13}C chemical shifts (δ in ppm) and coupling constants (*J* in Hz) in the major (M) and minor (m) geometrical isomers of compounds 6a-6c.

Compound	Isomer (%)	^{1}H-NMR			^{13}C-NMR
		H-2 ($^{3}J_{HP}$, $^{3}J_{HH}$)	CO_2R	OR	C-2 ($^{2}J_{CP}$)
6a	M (68)	3.35 (15.1, 10.2)	3.84	3.20	63.2 (15.0)
	m (32)	3.21 (16.1, 9.1)	3.83	3.60	61.9 (15.0)
6b	M (66)	3.21 (16.1, 9.1)	4.10-4.22[a]	3.67-3.81[a]	62.2 (14.0)
	m (34)	3.21 (16.1, 9.1)	4.23–4.35[a]	3.93–4.12[a]	61.8 (15.3)
6c	M (75)	3.75 (15.2, 8.2)	1.49	0.25	63.3 (15.0)
	m (25)	2.92 (17.3, 10.1)	1.28	1.33	62.3 (15.5)

[a] *The methylene group of OR moiety*

*Dimethyl 3-(triphenylphosphoranyieldne)-2-(4-phenylthiosemicarbazido)succinate (**4a**)*

Pale brown powder; yield: 1.10 g (96%); mp 126-127 °C. IR (KBr): $\bar{\upsilon}$ = 3287, 3237 (NH); 1750, 1633 (C=O); 1148 (C=S) cm^{-1}. Anal. calc. for $C_{31}H_{30}N_3O_4PS$ (571.64): C, 65.14; H, 5.29; N, 7.35%; found: C, 64.95; H, 5.36; N, 6.92%. NMR data for the major isomer (64%): ^{1}H-MMR: δ=3.17 (s, Me), 3.24 (*dd*, $^{3}J_{HP}$ = 15.3, $^{3}J_{HH}$ = 9.0, CH), 3.79 (s, Me), 5.35 (*d* , $^{3}J_{HH}$ = 9.0, NH), 7.10-7.78 (*m*, 20 CH, NH), 9.24 (s, NH). ^{13}C-NMR: δ = 41.4 (*d*, $^{1}J_{CP}$ = 125.6, C=P), 49.7 (Me), 52.8 (Me), 63.1 (*d*, $^{2}J_{CP}$ = 14.8, CH), 123.3 (2 CH_{ortho} of Ph-N), 125.3 (CH_{para} of Ph-N), 126.6 (*d*, $^{1}J_{CP}$ = 91.9,3 C_{ipso} of Ph groups), 128.9 (2 CH_{meta} of Ph-N), 129.4 (*d*, $^{3}J_{CP}$ = 12.1, 6 CH_{meta} of Ph groups), 132.8 (*d*, $^{4}J_{CP}$ = 2.4, 3 CH_{para} of Ph groups),134.0 (*d*, $^{2}J_{CP}$ = 9.7, 6 CH_{ortho} of Ph groups), 138.8 (C_{ipso} of Ph-N), 170.4 (*d*, , $^{2}J_{CP}$ = 12.5, C=O), 174.3 (*d*, $^{3}J_{CP}$ = 9.4, C=O), 179.9 (C=S). NMR data for the minor isomer (36%): ^{1}H-MMR: δ = 3.49 (*dd*, $^{3}J_{HP}$ = 13.3, $^{3}J_{HH}$ = 6.3, CH), 3.59 (s, Me), 3.77 (s, Me), 4.97 (*br.d* , $^{3}J_{HH}$ = 9.2, NH), 7.10-7.78 (*m*, 20 CH, NH), 9.18 (s, NH). ^{13}C-NMR: δ = 41.4 (*d*, $^{1}J_{CP}$ = 125.6, C=P), 50.6 (Me), 52.7 (Me), 62.4 (*d*, $^{2}J_{CP}$ = 15.1, CH), 123.3 (2 CH_{ortho} of Ph-N), 125.5 (CH_{para} of Ph-N), 126.1 (*d*, $^{1}J_{CP}$ = 92.3, 3 C_{ipso} of Ph groups), 129.0 (2 CH_{meta} of Ph-N), 129.4 (*d*, $^{3}J_{CP}$ = 12.1, 6 CH_{meta} of Ph groups), 132.8 (*d*, $^{4}J_{CP}$ = 2.4, 3 CH_{para} of Ph groups),134.0 (*d*, $^{2}J_{CP}$ = 9.7, 6 CH_{ortho} of Ph groups), 138.7 (C_{ipso} of Ph-N), 170.4 (*d*, , $^{2}J_{CP}$ = 12.5, C=O), 174.3 (d, $^{3}J_{CP}$ = 9.4, C=O), 179.9 (C=S). EI-MS: 571 (<1, M^{+}), 333 (3), 303 (6), 275 (4), 228 (2), 185 (34), 183 (82), 165 (33), 152 (22), 111 (56), 107 (32), 91 (21), 77 (100), 59 (12), 52 (32).

*Diethyl 3-(triphenylphosphoranyieldne)-2-(4-phenylthiosemicarbazido)succinate (**4b**)*

Pale yellow powder; yield: 1.13 g (94%); mp 118-119 °C. IR (KBr): $\bar{\upsilon}$ = 3343, 3286 (NH); 1743, 1626 (C=O); 1146 (C=S) cm^{-1}. Anal.

calc. for $C_{33}H_{34}N_3O_4PS$ (599.69): C, 66.09; H, 5.71; N, 7.01%; found: C, 65.90; H, 5.69; N, 7.39%. NMR data for the major isomer (64%): ^{1}H-MMR: δ = 0.47 (*t*, $^3J_{HH}$ = 7.1, Me), 1.31 (t, $^3J_{HH}$ = 7.2, Me), 3.21 (*dd*, $^3J_{HP}$ = 16.1, $^3J_{HH}$ = 9.1, CH), 3.67-3.81 (complex (AB)X_3 system, CH_2), 4.10-4.22 (complex (AB)X_3 system, CH_2), 5.37 (*d*, $^3J_{HH}$ = 9.1, NH), 7.08-7.79 (*m*, 20 CH, NH), 9.29 (s, NH). ^{13}C-NMR: δ = 14.3 (Me), 14.7 (Me), 41.5 (*d*, $^1J_{CP}$ = 122.6, C=P), 58.3 (CH2), 61.7 (CH_2), 62.9 (*d*, $^2J_{CP}$ = 14.9, CH), 123.3 (2 CH_{ortho} of Ph-N), 125.3 (CH_{para} of Ph-N), 126.8 (*d*, $^1J_{CP}$ = 92.1, 3 C_{ipso} of Ph groups), 128.9 (2 CH_{meta} of Ph-N), 129.3 (*d*, $^3J_{CP}$ = 12.3, 6 CH_{meta} of Ph groups), 132.7 (*d*, $^4J_{CP}$ = 2.6, 3 CH_{para} of Ph groups),134.1 (*d*, $^2J_{CP}$ = 9.7, 6 CH_{ortho} of Ph groups), 138.8 (C_{ipso} of Ph-N), 169.9 (*d*, , $^2J_{CP}$ = 13.5, C=O), 173.8 (*d*, $^3J_{CP}$ = 8.6, C=O), 179.9 (C=S). NMR data for the minor isomer (33%): ^{1}H-MMR: δ = 1.21 (t, $^3J_{HH}$ = 7.1, Me), 1.34 (t, $^3J_{HH}$ = 7.0, Me), 3.21 (dd , $^3J_{HP}$ = 16.1, $^3J_{HH}$ = 9.1, CH), 3.93-4.12 (complex (AB)X_3 system, CH_2), 4.23-4.35 (complex (AB)X_3 system, CH_2), 5.01 (br.d, $^3J_{HH}$ = 9.5, NH), 7.08-7.79 (*m*, 20 CH, NH), 9.22 (s, NH). ^{13}C-NMR: δ = 14.7 (Me), 15.4 (Me), 41.5 (*d*, $^1J_{CP}$ = 122.6, C=P), 58.9 (CH_2), 61.7 (CH_2), 61.9 (*d*, $^2J_{CP}$ = 15.7, CH), 123.3 (2 CH_{ortho} of Ph-N), 125.5 (CH_{para} of Ph-N), 126.2 (*d*, $^1J_{CP}$ = 90.2, 3 C_{ipso} of Ph groups), 129.0 (2 CH_{meta} of Ph-N), 129.4 (d, $^3J_{CP}$ = 11.5, 6 CH_{meta} of Ph groups), 132.6 (d, $^4J_{CP}$ = 3.0, 3 CH_{para} of Ph groups),133.4 (*d*, $^2J_{CP}$ = 9.8, 6 CH_{ortho} of Ph groups), 138.7 (C_{ipso} of Ph-N), 169.9 (*d*, , $^2J_{CP}$ = 13.5, C = O), 173.8 (*d*, $^3J_{CP}$ = 8.6, C=O), 179.9 (C=S). EI-MS: 599 (<1, M+), 483 (3), 450 (2), 374 (11), 276 (44), 275 (86), 262 (32), 261 (10), 205 (30), 185 (50), 183 (100), 152 (44), 135 (22), 110 (35), 108 (42), 91 (26), 78 (40), 77 (100), 52 (84), 42 (16).

Di-tert-butyl 3-(triphenylphosphoranyieldne)-2-(4-phenylthiosemicarbazido)succinate (4c)

White powder; yield: 0.96 g (73%); mp 149-150 °C. IR (KBr): $\bar{\upsilon}$= 3302, 3279 (NH); 1718, 1615 (C=O); 1143 (C=S) cm^{-1}. Anal. calc. for $C_{37}H_{42}N_3O_4PS$ (655.8): C, 67.77; H, 6.46; N, 6.41%; found: C, 67.73; H, 6.45; N, 6.65%. NMR data for the major isomer (76%): ^{1}H-MMR: δ = 0.95 (s, CMe_3), 1.54 (s, CMe_3), 3.03 (dd, $^3J_{HP}$ = 15.9, $^3J_{HH}$ = 8.5, CH), 5.29 (d, $^3J_{HH}$ = 8.5, NH), 7.07-7.78 (*m*, 20 CH, NH), 9.29 (s, NH). ^{13}C-NMR: = 28.7 (2 CMe™), 41.3 (*d*, $^1J_{CP}$ = 125.8, C=P), 63.3 (d, $^2J_{CP}$ = 15.5, CH), 66.3 (2 CMe3), 123.2 (2 CH_{ortho} of Ph-N), 125.1 (CH_{para} of Ph-N), 127.4 (d, $^1J_{CP}$ = 92.0, 3 C_{ipso} of Ph groups), 128.8 (2 CH_{meta} of Ph-N), 129.1 (*d*, $^3J_{CP}$ = 12.2, 6 CH_{meta} of Ph groups), 132.6 (*d*, $^4J_{CP}$ = 2.7, 3 CH_{para} of Ph groups), 134.1 (d, $^2J_{CP}$ = 9.7, 6 CH_{ortho} of Ph groups), 138.9 (C_{ipso} of Ph-N), 169.5 (d, $^2J_{CP}$ = 12.0, C=O), 173.5 (*d*, $^3J_{CP}$ = 9.3, C=O), 179.8 (C=S). NMR data for the minor isomer (24%): ^{1}H-MMR: δ = 1.46 (s, CMe_3), 1.51 (s, CMe_3), 2.92 (*dd*, $^3J_{HP}$ = 17.3, $^3J_{HH}$ = 10.1, CH), 5.10 (br.d, $^3J_{HH}$ = 9.9, NH), 7.07-7.78 (*m* , 20 CH, NH), 9.22 (s, NH). ^{13}C-NMR: δ = 29.3 (2 CMe_3), 41.3 (d, $^1J_{CP}$ =

125.8, C=P), 62.2 (*d*, $^2J_{CP}$ = 16.7, CH), 66.8 (2 CMe3), 123.4 (2 CH_{ortho} of Ph-N), 125.4 (CH_{para} of Ph-N), 126.6 (*d*, $^1J_{CP}$ = 92.4, 3 C_{ipso} of Ph groups), 128.9 (2 CH_{meta} of Ph-N), 129.2 (d, $^3J_{CP}$ = 11.9, 6 CH_{meta} of Ph groups), 132.6 (d, $^4J_{CP}$ = 2.7, 3 CH_{para} of Ph groups), 134.0 (*d*, $^2J_{CP}$ = 9.6, 6 CH_{ortho} of Ph groups), 138.8 (C_{ipso} of Ph-N), 169.5 (*d*, $^2J_{CP}$ = 12.0, C=O), 173.5 (d, $^3J_{CP}$ = 9.3, C=O), 179.8 (C=S). EI-MS: 655 (<1, M^+), 486 (2), 320 (10), 319 (50), 303 (24), 262 (44), 261 (12), 185 (30), 183 (100), 178 (100), 152 (22), 136 (40), 109 (29), 93 (24), 77 (81), 58 (100), 41 (60).

*Dimethyl 2-(2,4-dinitrophenylhydrazino)-3-(triphenylphosphoranyieldne)succinate (**6a**)*

Red brown powder; yield: 0.78 g (75%); mp 126-127 °C. IR (KBr): $\bar{\upsilon}$= 3311, 3250 (NH); 1720, 1618 (C=O); 1517, 1309 (NO_2) cm^{-1}. Anal. calc. for C30H27N4O8P (602.53): C, 59.80; H, 4.52; N, 9.30%; found: C, 59.85; H, 4.59; N, 9.32%. NMR data for the major isomer (68%): ^{1}H-MMR: δ = 3.20 (s, Me), 3.35 (*dd*, $^3J_{HP}$ = 15.1, $^3J_{HH}$ = 10.2, CH), 3.84 (s, Me), 5.59 (*d* , $^3J_{HH}$ = 10.2, NH), 7.37 (*d* , $^3J_{HH}$ = 9.5, CH), 7.50-7.71 (m, 15 CH), 8.02 (*d* , $^3J_{HH}$ = 9.5, CH), 9.04 (s , CH), 9.97 (s, NH). ^{13}C-NMR: = 40.7 (*d*, $^1J_{CP}$ = 126, C=P), 52.2 (Me), 53.4 (Me), 62.3 (*d*, $^2J_{CP}$ = 15, CH), 115.7 (CH_{ortho} of Ph-N) 123.7 (CH_{meta} of Ph-N),), 126.1(*d*, $^1J_{CP}$ = 92, 3 C_{ipso} of Ph groups), 128.7 (Cortho of Ph-N), 128.8 (*d*, $^3J_{CP}$ = 12, 6 CH_{meta} of Ph groups), 129.3 (CH_{meta} of Ph-N), 132.3 (6 CH_{para} of Ph groups),133.5 (*d*, $^2J_{CP}$ = 9, 6 CH_{ortho} of Ph groups), 135.8 (Cpara of Ph-N),149.3 (C_{ipso} of Ph-N), 169.9 (*d*, $^2J_{CP}$ = 13, C=O), 174.1 (*d*, , $^3J_{CP}$ = 8, C=O). NMR data for the minor isomer (32%): ^{1}H-MMR: = 3.43 (*dd*, $^3J_{HP}$ = 17.2, $^3J_{HH}$ = 9.6, CH), 3.60 (s, Me), 3.83 (s, Me), 5.06 (d , $^3J_{HH}$ = 9.2, NH), 7.37 (d , $^3J_{HH}$ = 9.5, CH), 7.50-7.71 (m, 15 CH), 8.02 (d , $^3J_{HH}$ = 9.5, CH), 9.04 (s , CH), 10.03 (s, NH). ^{13}C-NMR: δ = 41.8 (*d*, $^1J_{CP}$ = 125, C=P), 49.2 (Me), 50.1 (Me), 61.9 (*d*, $^2J_{CP}$ = 15, CH), 115.7 (CH_{ortho} of Ph-N) 123.7 (CH_{meta} of Ph-N),), 125.7 (*d*, $^1J_{CP}$ = 92, 3 C_{ipso} of Ph groups), 128.7 (Cortho of Ph-N), 128.8 (*d*, $^3J_{CP}$ = 12, 6 CH_{meta} of Ph groups), 129.3 (CH_{meta} of Ph-N), 132.3 (6 CH_{para} of Ph groups),133.5 (*d*, $^2J_{CP}$ = 9, 6 CH_{ortho} of Ph groups), 135.8 (Cpara of Ph-N), 149.4 (C_{ipso} of Ph-N), 169.9 (*d*, $^2J_{CP}$ = 13, C=O), 174.8 (*d*, $^3J_{CP}$ = 10, C=O). EI-MS: 602 (<1, M^+), 585 (4), 570 (4), 555 (4), 181 (10), 166 (15), 142 (8), 125 (2), 120 (3), 76 (100), 52 (23).

*Diethyl 2-(2,4-dinitrophenylhydrazino)-3-(triphenylphosphoranyieldne)succinate (**6b**)*

Red brown powder; yield: 0.68 g (64%); mp 118-119 °C. IR (KBr): $\bar{\upsilon}$= 3340, 3286 (NH); 1731, 1619 (C=O); 1519, 1333 (NO_2) cm^{-1}. Anal. calc. for $C_{32}H_{31}N_4O_8P$ (630.58): C, 60.95; H, 4.96; N, 8.88%; found: C, 60.90; H, 4.90; N, 8.99%. NMR data for the major isomer (66%): ^{1}H-MMR: δ = 0.51 (t, $^3J_{HH}$ = 7.0, Me), 1.31 (t, $^3J_{HH}$ = 7.2, Me), 3.21 (dd, $^3J_{HP}$ = 16.1, $^3J_{HH}$ = 9.1, CH), 3.67-3.81 (complex (AB)X_3 system, CH_2), 4.10-4.22 (complex (AB)X_3 system, CH_2), 5.10

(*d* , $^{3}J_{HH}$ = 10.2, NH), 7.40 (*d* , $^{3}J_{HH}$ = 9.6, CH), 7.59-7.73 (*m*, 15 CH), 8.03 (*dd* , $^{3}J_{HH}$ = 9.5, $^{4}J_{HH}$ = 2.1 CH), 9.03 (*d* , $^{4}J_{HH}$ = 2.1, CH), 10.82 (s, NH).^{13}C-NMR: δ = 13.8 (Me), 14.1 (Me), 41.3 (*d*, $^{1}J_{CP}$ = 127, C=P), 57.8 (CH_2), 61.2 (CH_2), 62.2 (*d*, $^{2}J_{CP}$ = 14, CH), 115.5 (CH_{ortho} of Ph-N) 123.7 (CH_{meta} of Ph-N),), 126.3(*d*, $^{1}J_{CP}$ = 92, 3 C_{ipso} of Ph groups), 128.7 (Cortho of Ph-N), 128.8 (*d*, $^{3}J_{CP}$ = 12, 6 CH_{meta} of Ph groups), 129.3 (CH_{meta} of Ph-N), 132.3 (6 CH_{para} of Ph groups),133.5 (d, $^{2}J_{CP}$ = 9, 6 CH_{ortho} of Ph groups), 135.8 (Cpara of Ph-N),149.4 (C_{ipso} of Ph-N), 169.5 (*d*, , $^{2}J_{CP}$ = 12, C=O), 173.8 (*d*, $^{3}J_{CP}$ = 9, C=O). NMR data for the minor isomer (34%): ^{1}H-MMR: δ = 1.21 (*t*, $^{3}J_{HH}$ = 7.1, Me), 1.34 (*t*, $^{3}J_{HH}$ = 7.0, Me), 3.21 (dd , $^{3}J_{HP}$ = 16.1, $^{3}J_{HH}$ = 9.1, CH), 3.93-4.12 (complex (AB)X3 system, CH_2), 4.23-4.35 (complex (AB)X3 system, CH_2), 5.60 (*d* , $^{3}J_{HH}$ = 10.2, NH), 7.40 (*d* , $^{3}J_{HH}$ = 9.6, CH), 7.59-7.73 (m, 15 CH), 8.03 (*dd* , $^{3}J_{HH}$ = 9.5, $^{4}J_{HH}$ = 2.1 CH), 9.03 (*d* , $^{4}J_{HH}$ = 2.1, CH), 10.01 (s, NH). ^{13}C-NMR: δ = 14.0 (Me), 14.9 (Me), 41.9 (d, $^{1}J_{CP}$ = 127, C=P), 58.4 (CH_2), 61.7 (CH_2), 61.8 (d, $^{2}J_{CP}$ = 15.3, CH), 115.5 (CH_{ortho} of Ph-N) 123.7 (CH_{meta} of Ph-N),), 125.8 (*d*, $^{1}J_{CP}$ = 92, 3 C_{ipso} of Ph groups), 128.7 (Cortho of Ph-N), 128.8 (*d*, $^{3}J_{CP}$ = 12, 6 CH_{meta} of Ph groups), 129.3 (CH_{meta} of Ph-N), 132.3 (6 CH_{para} of Ph groups),133.5 (*d*, $^{2}J_{CP}$ = 9, 6 CH_{ortho} of Ph groups), 135.8 (Cpara of Ph-N), 149.4 (C_{ipso} of Ph-N), 169.5 (*d*, , $^{2}J_{CP}$ = 12, C=O), 174.5 (*d*, $^{2}J_{CP}$ = 9, C=O). EI-MS: 630 (<1, M^{+}), 613 (4), 584 (4), 181 (10), 166 (15), 164 (5), 142 (54), 76 (100), 52 (24), 45 (4), 44 (4), 31 (2).

*Di-tert-butyl-2-(2,4-dinitrophenylhydrazino)-3-(triphenylphosphoranyieldne)succinate (**6c**)*

Red brown; yield: 0.96 g (58%); mp 149-150 °C. IR (KBr): $\bar{\upsilon}$= 3321, 3200 (NH); 1710, 1617 (C=O); 1517, 1312 (NO_2) cm^{-1}. Anal. calc. for $C_{36}H_{39}N_4O_8P$ (686.69): C, 62.97; H, 5.72; N, 8.16%; found: C, 62.89; H, 5.68; N, 8.12%. NMR data for the major isomer (75%): ^{1}H-MMR: δ = 1.49 (s, CMe_3), 1.25 (s, CMe_3), 3.75 (*dd*, $^{3}J_{HP}$ = 15.2, $^{3}J_{HH}$ = 8.2, CH), 6.67 (*d* , $^{3}J_{HH}$ = 9.2, NH), 7.44-7.96 (*m*, 15 CH), 7.96 (d , $^{3}J_{HH}$ = 9.7, CH), 8.30 (dd , $^{3}J_{HH}$ = 9.7, $^{4}J_{HH}$ = 2.5, CH), 9.10 (d , $^{4}J_{HH}$ = 2.5, CH), 11.04 (s, NH). ^{13}C-NMR: δ = 28.6 (2 CMe_3), 41.7 (d, $^{1}J_{CP}$ = 125.2, C=P), 63.3 (d, $^{2}J_{CP}$ = 15, CH), 65.3 (2 CMe_3) 115.3 (CH_{ortho} of Ph-N) 122.5 (CH_{meta} of Ph-N),), 127.4(*d*, $^{1}J_{CP}$ = 92, 3 C_{ipso} of Ph groups), 127.5 (Cortho of Ph-N), 128.2 (*d*, $^{3}J_{CP}$ = 12.2, 6 CH_{meta} of Ph groups), 129.0 (CH_{meta} of Ph-N), 130.9 (6 CH_{para} of Ph groups),131.0 (d, $^{2}J_{CP}$ = 9.2, 6 CH_{ortho} of Ph groups), 133.5 (Cpara of Ph-N),148.3 (C_{ipso} of Ph-N), 169.2 (*d*, $^{2}J_{CP}$ = 13, C=O), 173.1 (d, , $^{3}J_{CP}$ = 8, C=O). NMR data for the minor isomer (25%): ^{1}H-MMR: = 1.28 (s, CMe_3), 1.33 (s, CMe_3), 3.53 (*dd*, $^{3}J_{HP}$ = 16.2, $^{3}J_{HH}$ = 9.5, CH), 5.96 (*d* , $^{3}J_{HH}$ = 8.2, NH), 7.44-7.96 (*m*, 15 CH), 7.96 (*d* , $^{3}J_{HH}$ = 9.7, CH), 8.30 (*dd* , $^{3}J_{HH}$ = 9.7, $^{4}J_{HH}$ = 2.5, CH), 9.10 (*d* , $^{4}J_{HH}$ = 2.5, CH), 11.64 (s, NH). ^{13}C-NMR: δ = 28.3 (2 CMe_3), 41.7 (*d*, $^{1}J_{CP}$ = 125.2, C=P), 62.3 (*d*,

$^{2}J_{CP}$ = 15.5, CH), 65.9 (2 CMe_3) 115.4 (CH_{ortho} of Ph-N) 122.6 (CH_{meta} of Ph-N),), 126.4(d, $^{1}J_{CP}$ = 92.4, 3 C_{ipso} of Ph groups), 127.9 (Cortho of Ph-N), 128.1 (d, $^{3}J_{CP}$ = 12.2, 6 CH_{meta} of Ph groups), 129.1 (CH_{meta} of Ph-N), 130.9 (6 CH_{para} of Ph groups),132.0 (d, $^{2}J_{CP}$ = 9.5, 6 CH_{ortho} of Ph groups), 133.7 (Cpara of Ph-N),148.3 (C_{ipso} of Ph-N), 169.5 (d, $^{2}J_{CP}$ = 12, C=O), 172.8 (*d*, , $^{3}J_{CP}$ = 8, C=O). EI-MS: 686 (<1, M^{+}), 669 (6), 639 (5), 630 (2), 612 (5), 181 (14), 166 (20), 164 (7), 142 (10), 125 (2), 76 (100), 59 (9), 52 (100), 50 (31), 52 (5)

Conclusion

In conclusion, the present method may be used as a practical route for the synthesis of these stable phosphorus yields under neutral conditions and starting materials can be mixed without any activation or modification. This procedure has advantages of high yields, mild reaction conditions, and simple experimental and work-up conditions.

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