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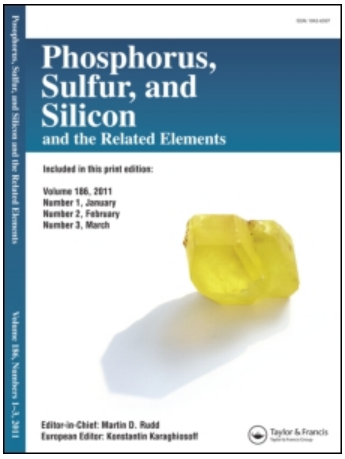

Phosphorus, Sulfur, and Silicon and the Related Elements

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Sayyed Mostafa Habibi-Khorassani[a]; Ali Ebrahimi[a]; Malek Taher Maghsoodlou[a]; Faramarz Rostami Charati[b]; Mohammad Amin Kazemian[a]; Pouya Karimi[a]

[a] Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, Iran [b] High Education Center, Gorgan University of Agricultural Sciences and Natural Resources, Gonbad, Iran

Online publication date: 24 February 2010

To cite this Article Habibi-Khorassani, Sayyed Mostafa , Ebrahimi, Ali , Maghsoodlou, Malek Taher , Charati, Faramarz Rostami , Kazemian, Mohammad Amin and Karimi, Pouya(2010) 'A Facile Synthesis and Theoretical Study of Novel Stable Heterocyclic Phosphorus Ylides Containing a 2,4-Dimethyl-3-acetyl Moiety', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 3, 559 — 566

To link to this Article: DOI: 10.1080/10426500902845753

URL: http://dx.doi.org/10.1080/10426500902845753

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Phosphorus, Sulfur, and Silicon, 185:559–566, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902845753

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A FACILE SYNTHESIS AND THEORETICAL STUDY OF NOVEL STABLE HETEROCYCLIC PHOSPHORUS YLIDES CONTAINING A 2,4-DIMETHYL-3-ACETYL MOIETY

Sayyed Mostafa Habibi-Khorassani,[1] Ali Ebrahimi,[1] Malek Taher Maghsoodlou,[1] Faramarz Rostami Charati,[2] Mohammad Amin Kazemian,[1] and Pouya Karimi[1]

[1]Department of Chemistry, The University of Sistan and Baluchestan, Zahedan, Iran

[2]High Education Center, Gorgan University of Agricultural Sciences and Natural Resources, Gonbad, Iran

A general and practical route has been considered for the synthesis of stable heterocyclic phosphorus ylides 3a–c by a one-pot condensation reaction between dialkyl acetylenedicarboxylate and triphenylphosphine in the presence of -NH heterocyclic compounds such as 2,4-dimethyl-3-acetyl pyrrole. The stable ylides 3a–b exist in solution as a mixture of the two isomers, while 3c indicates only one isomer. For this reason, the assignments of more stable Z- or E-isomers as the major or minor forms were investigated using the theoretical calculations.

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Keywords 2,4-Dimethyl-3-acetyl pyrrole; intramolecular hydrogen bond; stable phosphorus ylides; theoretical calculations; triphenylphosphine; *Z*- or *E*-isomers

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INTRODUCTION

Pyrrole derivatives as heterocyclic organophosphorus compounds are important intermediates, not only for the synthesis of drugs, pigments, and pharmaceuticals, but also for the development of organic functional groups.[1] Pyrroles occur in numerous pharmacologically active natural and unnatural products. Functionalized pyrroles represent building blocks of natural tetrapyrrole pigments, such as porphobilinogen or bilirubin, and of various other natural products and their analogues.[2,3] Morever, the pyrrole zomepirac possesses analgesic and antiphlogistic activity and has found clinical applications.[2] Substituted oligopyrroles

Received 27 January 2009; accepted 10 February 2009.

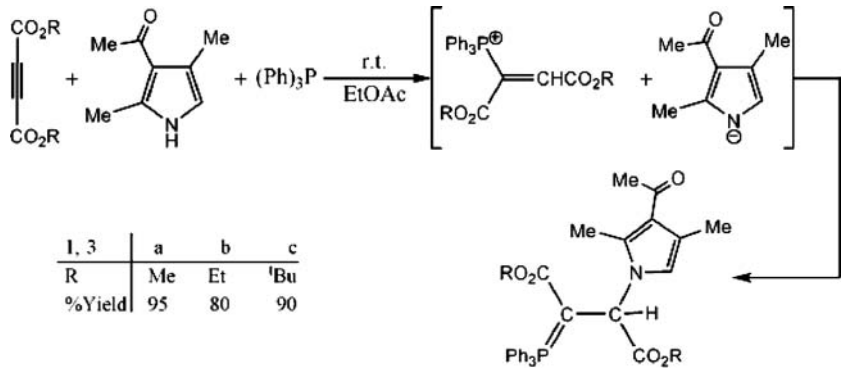
We gratefully acknowledge the financial support from the Research Council of Sistan & Baluchestan University and Gorgan University of Agricultural Sciences and Natural Resources.

Address correspondence to Sayyed Mostafa Habibi-Khorassani, Department of Chemistry, The University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran. E-mail: smhabibius@yahoo.com

are of interest in the field of material sciences.[2,3] With respect to the importance of heterocyclic organophosphorus compounds, the development of simple synthetic routes for widely used organic materials, and especially for organophosphorus compounds, from readily available reagents is one of the major tasks in organic synthesis.[4] Organophosphorous compounds are of particular interest as synthetic targets due to their importance in industrial, biological, and chemical syntheses.[4–10] Many strategies have appeared describing novel syntheses of organophosphorus compounds, including previous reports.[11–27] In this article, we report an efficient synthetic route to sterically congested nitrogen-containing phosphorus ylides **3a–c** using triphenylphosphine, dialkyl acetylenedicarboxylates **1**, and 2,4-dimethyl-3-acetyl pyrrole 2. In addition, an atoms–in-molecules (AIM) analysis at the HF/6-31G level of theory has been performed in order to gain a better understanding of the most geometrical parameters of both the *Z*-**3(a,c)** and the *E*-**3(a,c)** phosphorus ylides.

RESULTS AND DISCUSSION

The reaction between triphenylphosphine and dialkyl acetylenedicarboxylates **1(a, b,** or **c)** led to zwiterion **2**, which was followed by an attack by the nitrogen amine of the 2,4-dimethyl-3-acetyl pyrrole, to generate the phosphorus ylides *E*-**3** and *Z*-**3**. These reactions were carried out in diethyl ether at ambient temperature and were completed after approximately 6 h. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3** (Figure 1). No product other than **3** could be detected by NMR spectroscopy. The structures of compounds **3a–c** were deduced from the elemental analyses, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* value. The ^{1}H NMR spectrum (500 MHz) of **3a** displayed six singlets at $\delta = 1.42, 1.36, 2.04, 2.05, 2.13, 2.14$ ppm arising from methyl protons on pyrrole ring along with two methyl protons from two ester groups and two significant signals at $\delta = 6.7$ and 6.6 ppm from the hydrogen on C-5 of pyrrole ring for the major *Z*-**3a** and minor *E*-**3a** isomers, respectively. The aromatic protons (30 protons of six phenyl groups) appeared as a multiplet at $\delta = 7.20–7.38$. Although the presence of the ^{31}P nucleus has complicated both the ^{1}H and ^{13}C NMR spectra of **3a**, it helps in assignment of signals by long-range, spin–spin couplings with ^{1}H and ^{13}C nuclei. The ^{1}H and ^{13}C NMR



1, 3	a	b	c
R	Me	Et	^{t}Bu
%Yield	95	80	90

Figure 1 The reaction between triphenylphosphine, dialkyl acetylendicarboxylate **1** (**1a**, **1b**, or **1c**), and 2,4-dimethyl-3-acetyl pyrrole **2** for generating stable phosphorus ylide **3** (**3a**, **3b**, or **3c**).

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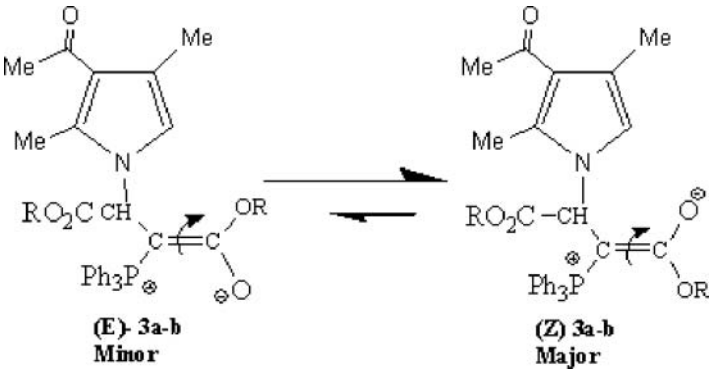

Figure 2 Two isomers (major and minor) of stable phosphorus ylides **3a–b**.

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spectra of **3b** are similar to those of **3a**, except for the signals from ester groups, which appear as characteristic resonance lines with the corresponding chemical shifts. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **3a** and **3b** showed the mixture of the two isomers (see Figure 2). The assignments of *E*-**3**(**a**,**b**) and *Z*-**3**(**a**,**b**) isomers as the major or minor forms in phosphorus ylides have been reported previously.[28–32] The ^{1}H NMR spectrum of **3a** exhibited two signals at 2.98 and 3.52 ppm arising from methoxy group in the *Z*-isomer, and two signals at 3.38 and 3.50 ppm for that in the *E*-isomer. The methyl group at 2.98 in the *Z*-isomer is shielded due to the anisotropic effect of a phenyl group of triphenylphosphine. This effect confirms why the *Z*-**3a** and *E*-**3a** isomers could appear as the major and minor forms, respectively, with the percentage of both isomers, as reported in the Experimental section. The signals for methine protons appeared as two doublets at $\delta = 4.24$ Hz ($^{3}J_{PH} = 4.43$) and $\delta = 4.29$ Hz ($^{3}J_{PH} = 5.50$), respectively, for the *Z*- and *E*- isomers. The ^{13}C NMR spectrum of **3a** exhibited 36 distinct resonances in a good agreement with the mixture of the two isomers. For the ^{13}C NMR spectroscopy, the anisotropic effect could not be reported for the methoxy group in the *Z*-isomer because of the small difference of their chemical shifts. The structural assignments made on the basis of the ^{1}H and ^{13}C NMR spectra of compounds **3a** and **3b** were supported by the IR spectra. The carbonyl region of these compounds **3a–b** exhibited absorption bands for each compound. The ester absorption is at 1600–1735 cm^{-1}, the conjugation of negative charge of the ylide moiety with the adjacent carbonyl group accounting for the reduction in frequency of the carbonyl bands, and allows determination of the ratio between the *E*- and *Z*-isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and rotation around the partial double bond in the *E*-**3(a,b)** and the (*Z*)-**3(a,b)** isomers (Figure 2) is slow on the NMR time scale at ambient temperature.

As can be seen in the Experimental section, the ^{13}C NMR spectrum of **3c** displays 11 distinct resonances, which is accord with only one isomer. This observation, presumably, is attributed to the steric factor of the bulky *tert*-butyl groups and more plausible intramolecular hydrogen bond in stable phosphorus ylides **3c** (see Figure S2 available online in the Supplemental Materials). On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[3–5] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the 2,4- dimethyl-3-acetyl **2** (see Figure 1).

THEORETICAL STUDY

Recently, different reports have been published on the synthesis of stable phosphorus ylides from the reaction between triphenylphosphine and reactive acetylenic esters in the presence of N—H, C—H, or S—H heterocyclic compounds. These ylides usually exist as a mixture of two isomers. The determination of a more stable isomer is impossible by the ^{31}P, ^{13}C, and ^{1}H NMR techniques. For this reason, theoretical study has been employed in order to gain a better understanding of the most important geometrical parameters and also relative energies of both isomers.

CALCULATIONS: STRUCTURE AND STABILITIES

In order to determine which is the more stable form of both *Z*-**3(a,c)** and *E*-**3(a,c)** isomer of the ylides (**3a** and **3c**), their structures were first optimized at the HF/6–31G level of theory[33] by Gaussian 98 program package.[34] Also the relative energies of the two isomers have been calculated at the HF/6–31G and B3LYP/6–311++G (d,p) levels (see Figures S1 and S2, Supplementary Materials). The relative stabilization energies for both *Z*-**3(a,c)** and *E*-**3(a,c)** isomers are reported in Table I. As can be seen, *Z*-**3a** and *Z*-**3c** isomers are more stable than *E*-**3a** and *E*-**3c** forms at the HF/6–31G and B3LYP/6–311++G(d,p) levels.

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Further investigations were undertaken in order to determine more effective factors on the stability of both isomers, on the basis of AIM calculations[35] at the HF/6–31G level of theory by the AIM2000 program package.[36] As noted in the literature,[37] the ranges of $\rho(r)$ and $\nabla^2\rho(r)$ are 0.002–0.035 e/a_0^3 and 0.024–0.139 e/a_0^5, respectively, if H-bonds exist. The number of hydrogen bonds in both categories (*E*-**3a** and *Z*-**3a**) and (*E*-**3c** and *Z*-**3c**) are 10 and 7 and also 14 and 12, respectively. In addition, the ranges of their electron densities are in 0.003–0.018 and 0.007–0.018 au and also 0.005–0.018 and 0.001–0.018 au), respectively. With respect to the large number of hydrogen bonds in both the *Z*- and the *E*-isomers, it is difficult to make a precise decision for determination of the more stable isomer. (See Figures S1 and S2, Supplemental Materials.)

On the basis of theoretical calculations (Table I), the difference between the relative stability of the *E*-**3a** and *Z*-**3a** isomers in gas phase is small (0.91 kcal/mol), while it is considerably greater in the *E*-**3c** and *Z*-**3c** (3.22 kcal/mol). Perhaps this noticeable difference is taken more in solution media for **3c** and, for this reason, it is possible to observe only one isomer of **3c** (*E* or *Z*). In the Experimental section, both the ^{1}H NMR and ^{13}C NMR spectroscopies indicated only one isomer for the **3c** ylide. Nevertheless, the result of our calculations is different for **3a** (observed as the two isomers), which may be attributed to the negligible difference in relative stability of the *E*-**3a** and the *Z*-**3a** isomers. Perhaps this negligible difference (0.67 or 0.91 kcal/mol) is not taken more considerably for **3a** in solution media, and for this reason it is possible to see the two isomers of **3a** (both *Z* and *E*

Table I The relative energy (kcal/mol) for *Z*- and *E*-isomers of ylides **3a** and **3c** calculated at HF/6–31G and B3LYP/6–311++G(d,p) levels

Conformer	HF	B3LYP
Z-**3a**	0.00	0.00
E-**3a**	0.67	0.91
Z-**3c**	0.00	0.00
E-**3c**	3.08	3.22

isomers). In recent case, the ^{1}H, ^{13}C, and ^{31}P NMR data exhibited the two isomers of ylide **3a**, which were consistent with the obtained result from the theoretical investigations.

CONCLUSION

In conclusion, we have prepared the novel stable phosphorus ylides using a one-pot reaction between triphenylphosphine and acetylenic compounds in the presence of a NH heterocyclic compound such as 2,4-dimethyl-3-acetyl pyrrole. The present method carries the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification. In addition, the assignments of the *Z* and *E* isomers as the major or minor forms in both of **3a** and **3c** ylides were undertaken by the theoretical study.

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, triphenylphosphine, and 2,4-dimethyl-3-acetyl pyrrole were obtained from Fluka (Buchs, Switzerland) and used without further purification. Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a Bruker DRX-500 Avance instrument with $CDCl_3$ as solvent at 500.1, 125.8, and 202.4 MHz, respectively. The mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Elemental analysis for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer.

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General Procedure for Preparation of the Ylides 3

To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 mmol) and 2,4-dimethyl-3-acetyl pyrrole (0.137 g, 1 mmol) in 5 mL of ethyl acetate, a solution of dialkyl acetylendicarboxylate(1 mmol) in 1 mL of ethyl acetate was added dropwise at $-5^{\circ}C$ over 10 min. The reaction mixture was allowed to warm up to room temperature and stirred for 1 h. The products **3a–c** were filtered and washed with (3×10 mL) cold diethyl ether. The characterization data of dialkyl 2-(2,4-dimethyl-3-acetyl pyrrole-1-yl)-3-(triphenylphosphoranilidene)butandioate (**3a–c**) are given below.

Dimethyl 2-(2,4-Dimethyl-3-acetyl pyrrole-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3a). The product of **3a** (*Z*) was obtained as pale orange powder, mp 146–148°C, and yield 95%. IR (ν_{max}, cm^{-1}): 1735 (C=O of acetyl), 1730 (C=O of ester), 1600 (C=C). MS (*m/z,%*): 510 (M−OCH_3, 5), 405 (M-($C_8H_{10}ON$-), 60), 279 (M−PPh_3, 20), 262 (PPh_3, 75), 77 (Ph, 25). Anal. Calcd for $C_{32}H_{32}NO_5P$ ($M_w = 541$), C, 70.97; H, 5.91; N, 2.58, Found: C, 71.3; H, 5.84; N, 2.63.

Major isomer (*Z*)-3a: (60%) ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.41 (3H, s, CH_3), 2.04 (3H, s, CH_3), 2.13 (3H, s, CH_3), 2.98, 3.52 (6H, s, 2 OCH_3), 4.24 (1H, d, $^{3}J_{PH} =$ 4.43 Hz, P−C−CH), 6.7 (1H, s, C_5 of pyrrole), 7.20–7.27 (15H, m, $3C_6H_5$), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 11.03, 14.4 and 22.9 (s, $3CH_3$ on pyrrole ring), 42.8 (d, $^{1}J_{PC} =$ 135 Hz, P−C), 49.4, 52.9 (s, 2 OCH_3), 58.6 (d, $^{2}J_{PC} = 16.1$ Hz, P−C−CH), 118.2, 118.9 and 120.8 (3C, of pyrrole ring), 126.4 (d, $^{1}J_{PC} = 92.1$ Hz, C_{ipso}), 129.1 (d, $^{3}J_{PC} = 4$ Hz, C_{meta}), 132.4 (s, C_{para}), 133.6 (d, $^{2}J_{PC} = 5.9$ Hz, C_{ortho}), 135.5 (s, C_2 of pyrrole ring), 169.8 (d, $^{2}J_{PC} = 12.9$ Hz, C=O), 172.3 (d, $^{3}J_{PC} = 6.5$ Hz, C=O), 196.0 (s, C=O of acetyl). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 24.2 (s, Ph_3P^{+}−C).

Minor isomer (*E*)-3: (40%),^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.36 (3H, s, CH_3), 2.05 (3H, s, CH_3), 2.14 (3H, s, CH_3), 3.38, 3.50 (s, 6H, $2OCH_3$), 4.29 (1H, d, $^{3}J_{PH}$ = 5.5 Hz, P−C−CH), 6.6 (1H, s, C_5 of pyrrole), 7.31–7.38 (15H, m, $3C_6H_5$), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 11.13, 14.6 and 23.1 (s, $3CH_3$ on pyrrole ring), 42.2 (d, $^{1}J_{PC}$ = 127.3 Hz, P−C), 50.47, 52.72 (s, 2 OCH_3), 58.2 (d, $^{2}J_{PC}$ = 16.3 Hz, P−C−CH), 118.04, 118.4 and 121.1 (3C, of pyrrole ring), 125.7 (d, $^{1}J_{PC}$ = 92.2 Hz, C_{ipso}), 128.9 (d, $^{3}J_{PC}$ = 3.9 Hz, C_{meta}), 132.3 (s, C_{para}), 133.5 (d, $^{2}J_{PC}$ = 5.8 Hz, C_{ortho}), 135.8 (s, C_2 of pyrrole ring), 170.5 (d, $^{2}J_{PC}$ = 17.7 Hz, C=O), 172.1 (d, $^{3}J_{PC}$ = 7.1 Hz, C=O), 195.9 (s, C=O of acetyl). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 24.9 (s, Ph_3P^+- C).

Diethyl 2-(2,4-Dimethyl-3-acetyl pyrrole-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3b). The product of **3b** (*Z*) was obtained as pale orange powder, mp 134–136°C, and yield 80%. IR (ν_{max}, cm^{-1}): 1735 (C=O of acetyl), 1730 (C=O of ester), 1600 (C=C), 1100 (C-O ether). MS (*m/z,%*): 443 (M-($C_8H_{10}ON$-), 50), 262 (PPh_3, 90), 77 (Ph, 25).Anal. Calcd for $C_{34}H_{36}NO_5P$ (M_w = 569), C, 71.73; H, 6.33; N, 2.46, Found: C, 71.85; H, 6.19; N, 2.66.

Major isomer (*Z*)-3b: (55%) ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.03, 1.38 (6H, t, $^{3}J_{HH}$ = 7.1 Hz, $2CH_3$), 2.04, 2.13 and 2.98, (9H, s, $3CH_3$ on pyrrole ring), 3.53 (2H, m, CH_2), 3.86 (2H, m, CH_2), 6.72 (1H, s, C_5 of pyrrole), 7.33–7.41 (15H, m, $3C_6H_5$), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 11.08, 14.9 and 23.2 (s, $3CH_3$ on pyrrole ring), 14.02, 14.26 (s, CH_3 of 2OEt), 41.91 (d, $^{1}J_{PC}$ = 127.6 Hz, P−C), 58.6 (d, $^{2}J_{PC}$ = 16.2 Hz, P−C−CH), 58.6, 61.52 (s, $2CH_2$ of OEt), 118.9, 119.0 and 120.74 (3C, of pyrrole ring), 126.6 (d, $^{1}J_{PC}$ = 91.9 Hz, C_{ipso}), 128.9 (d, $^{3}J_{PC}$ = 4.2 Hz, C_{meta}), 132.3 (s, C_{para}), 133.7 (d, $^{2}J_{PC}$ = 5.6 Hz, C_{ortho}), 135.6 (s, C_2 of pyrrole ring), 169.4 (d, $^{2}J_{PC}$ = 12.9 Hz, C=O), 171.6 (d, $^{3}J_{PC}$ = 13.13 Hz, C=O), 195.9 (s, C=O of acetyl). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 25.17 (s, Ph_3P^+- C).

Minor isomer (*E*)-3b: (45%), δ_H ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.9, 1.09 (6H, t, $^{3}J_{HH}$ = 7.1 Hz, $2CH_3$), 2.05, 2.15 and 3.4, (9H, s, $3CH_3$ on pyrrole ring), 3.55 (2H, m, CH_2), 3.89 (2H, m, CH_2), 6.68 (1H, s, C_5 of pyrrole), 7.21–7.27 (15H, m, $3C_6H_5$), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 11.17, 14.6 and 23.6 (s, $3CH_3$ on pyrrole ring), 14.23, 14.47 (s, CH_3 of 2OEt), 42.69 (d, $^{1}J_{PC}$ = 136 Hz, P−C), 58.1 (d, $^{2}J_{PC}$ = 15.8 Hz, P−C−CH), 58.5, 61.46 (s, $2CH_2$ of OEt), 117.88, 118.64 and 120.94 (3C, of pyrrole ring), 125.93 (d, $^{1}J_{PC}$ = 92.3 Hz, C_{ipso}), 128.4 (d, $^{3}J_{PC}$ = 4.1 Hz, C_{meta}), 132.2 (s, C_{para}), 133.5 (d, $^{2}J_{PC}$ = 5.4 Hz, C_{ortho}), 135.5 (s, C_2 of pyrrole ring), 170.3 (d, $^{2}J_{PC}$ = 18.03 Hz, C=O), 171.4 (d, $^{3}J_{PC}$ = 12.23 Hz, C=O), 195.7 (s, C=O of acetyl). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 25.0 (s, Ph_3P^+− C).

Di-tert-butyl 2-(2,4-Dimethyl-3-acetyl pyrrole-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3c). The product (*Z*)-**3c** was obtained as pale white powder, mp 160–162°C, and yield 90%. IR (ν_{max}, cm^{-1}): 1735 (C = O of acetyl), 1730 (C = O of esteres), 1600 (C = C). MS (*m/z,%*): 489 (M−($C_8H_{10}ON$−, 5), 423 (M−$2CO_2{}^tBu$, 5), 332 (M−$CO_2{}^tBu$−($C_8H_{10}ON$−), 25), 287 (M−$2CO_2{}^tBu$−($C_8H_{10}ON$−, 30), 77 (Ph, 8), 57 (^tBu, 75). Anal. Calcd for $C_{38}H_{44}NO_5P$ C, 72.96; H, 7.04; N, 2.24, Found: C, 73.18; H, 7.21; N, 2.33. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.9 (9H, s, ^tBu), 1.54 (9H, s, ^tBu), 1.57, 2.30 and 2.36 (9H, s, CH_3 on pyrrole ring), 4.33 (1H, d, $^{3}J_{PH}$ = 17.54 Hz, P−C−CH), 7.01 (1H, s, C_5 of pyrrole), 7.45–7.6 (15H, m, $3C_6H_5$), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 10,9, 14.6 and 22.8 (s, $3CH_3$ on pyrrole ring), 41.5 (d, $^{1}J_{PC}$ = 128 Hz, P−C), 58.9 (d, $^{2}J_{PC}$ = 16.7 Hz, P−C−CH), 77.6, 81.02 (s, 2 O−C), 117.9, 119.1 and 120.6 (3C, of pyrrole ring), 127.2 (d, $^{1}J_{PC}$ = 91.8 Hz, C_{ipso}), 128.7 (d, $^{3}J_{PC}$ = 12.23 Hz, C_{meta}), 132.1 (d, $^{4}J_{PC}$ = 2.8 Hz, C_{para}), 133.6 (d, $^{2}J_{PC}$ = 9.7 Hz, C_{ortho}), 135.4 (s, C_2 of pyrrole ring), 168.78 (d, $^{2}J_{PC}$ =

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12.4 Hz, C = O), 170.2 (d, $^3J_{PC}$ = 13.1 Hz, C = O), 195.8 (s, C = O of acetyl). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.7 (s, Ph_3P^+- C).

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