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A facile synthesis and theoretical study of novel stable heterocyclic phosphorus ylides containing 2,4-dimethyl-3-acetyl pyrrole

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Abstract: The reaction between dialkyl acetylenedicarboxylates and 2,4-dimethyl-3-acetyl pyrrole in presence of triphenylphosphine, in ethyl acetate, led to stable phosphorus ylides derivatives 3(a-c) in good yields. The stable ylides involving 3(a and b) exist in solution as a mixture of the two isomers, while 3c indicate only one isomer. For this reason, assignment of more stable Z or E isomers as a (major or minor) was investigated using theoretical calculations.

Keywords: Triphenylphosphine; Stable phosphorus ylides; Acetylenic ester; 2,4-Dimethyl-3-acetyl pyrrole; *Z* or *E* isomers; Intramolecular hydrogen bond; Theoretical calculations.

Introduction

Several pyrrole derivatives 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 analgetic and antiphlogistic activity has found clinical applications [2]. Substituted oligopyrroles 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 our previous reports [11-24]. Herein we report an efficient synthetic route to sterically congested nitrogen-containing phosphorus ylides **3** using triphenylphosphine, dialkyl acetylenedicarboxylates **1** and 2,4-dimethyl-3-acetyl pyrrole **2** (Figure 1).
In addition, atoms in molecules (AIM) analysis at HF/6-31G level of theory have been performed in order to gain a better understanding of most geometrical parameters of both ***Z*-3(a, c)** and ***E*-3(a, c)** of phosphorus ylides.

Results and Discussion

The reaction between triphenyl phosphine and dialkyl acetylenedicarboxylates **1**(**1a**, **1b** or **1c**) led to zwiter ion **2**, which was subsequently followed by nitrogen anion of the 2,4-dimethyl-3-acetyl pyrrole for generation of phosphorus ylides ***E*-3** and ***Z*-3** in ethyl acetate at ambient temperature. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**. Assignment of ***E*-3**(**a** and **b**) and ***Z*-3**(**a** and **b**) isomers as the major or minor form in phosphorus ylides have been previously reported in the

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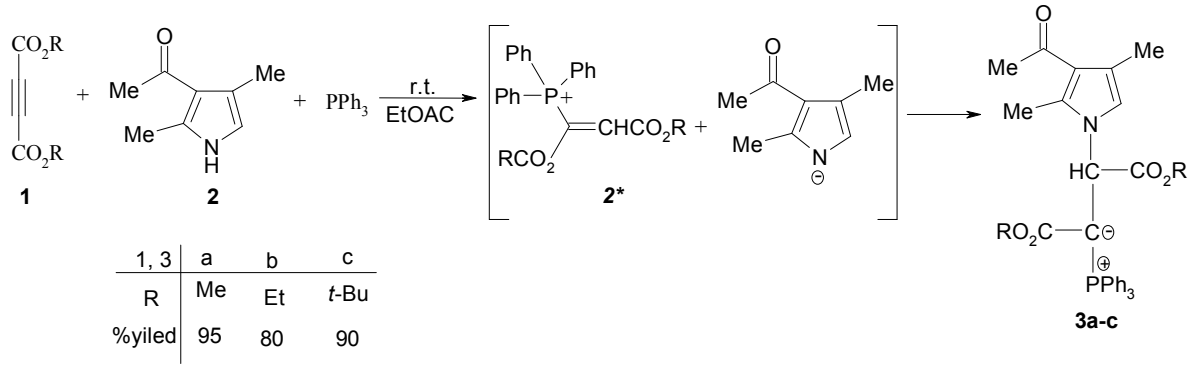
Figure 1. The reaction between triphenylphosphine, dialkyl acetylendicarboxylate 1 (1a, 1b or 1c) and 2,4-dimethyl-3-acetyl pyrrole 2 for generation of stable phosphorus ylide 3 (3a, 3b or 3c)



1, 3	a	b	c
R	Me	Et	*t*-Bu
%yiled	95	80	90

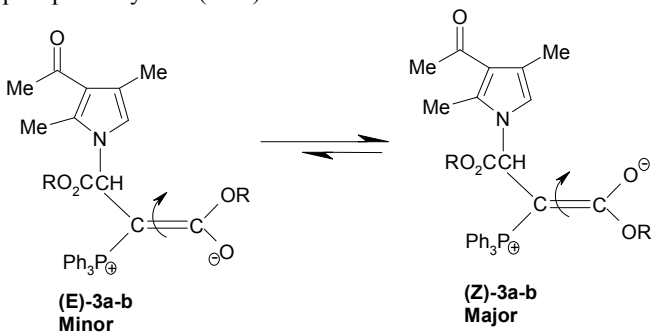
literature [25-29]. The ^{1}H NMR spectrum of **3a** exhibited two signals at 2.98 and 3.52 ppm arising from methoxy groups in the *Z*- isomer and two signals at 3.38 and 3.50 ppm for methoxy group in the *E*- isomer. The shift at 2.98 of methyl group in the *Z*- isomer is shielded duo to the anisotropic 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 respect to experimental abundance percentage of both isomers which have been reported in experimental section. Also signals for methine protons appeared as two doublet at δ=4.24 ppm (^{3}JPH=4.43) and δ=4.29 ppm (^{3}JPH=5.50), for the *Z*- and *E*- isomers respectively.

The structures of compounds **3a-c** were deduced from their IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. The mass spectra of these were not displayed molecular ion peaks at m/z value. The ^{1}H NMR spectra (300 MHz) of compound **3a** displayed six singlets (at δ=1.36, 1.42, 2.05, 2.04, 2.13, 2.14) arising from methyl protons on pyrrole ring along with two methyl protons from two ester groups. The hydrogen on C-5 of pyrrole ring exhibited two singlet at δ=6.7 and 6.6 for the major *Z*- and minor *E*- isomers, respectively. The aromatic protons (thirty protons of six phenyl groups) appeared as a multiplet at δ=7.20-7.38. The ^{13}C NMR spectrum of **3a** exhibited 36 distinct resonances that are in a good agreement with the mixture of the two isomers. The ^{1}H and ^{13}C NMR spectra of **3b** are similar to that of **3a**, except for the signals from ester groups, which appear as characteristic resonance lines with the corresponding chemical shifts (see Experimental section).

The ^{1}H and ^{13}C NMR spectra of compounds **3a** and **3b** are consistent with the two geometrical isomers. 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, **3(a** and **b)** exhibited two distinct absorption bands for each compound (see experimental section). Of special interest is the ester absorption at 1600-1735cm^{-1}. Conjugation of the negative charge of the ylide moiety with the adjacent carbonyl group accounts for the reduction of the wave numbers of the carbonyl absorption bands.

The ylide moieties of these compounds are strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in the ***E*-3(a** and **b)** and ***Z*-3(a, b)** isomers (Figure 2) are slow on the NMR timescale at ambient temperature.

Figure 2: Two isomers (major and minor) of stable phosphorus ylides (3a-b)



As can be seen in experimental section, the ^{13}C NMR spectrum of **3c** displays eleven distinct resonances which is accordance with only one isomer. Only one geometrical isomer was observed for di-*t*-butyl derivatives of **3c**, presumably, the more steric factor of the bulky *t*-butyl groups accompanied by intramolecular hydrogen bond critical points within the structure of

ylide **3c** which will be fully argued in the theoretical study section, both together would tend to dominate only the ***Z*-3c** isomer.

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 Figure1).

Experimental

Dialkyl acetylenedicarboxylates, triphenylphosphine, 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. Also, 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. In addition, 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.

General procedure for preparation of the ylides **3:** To a magnetically stirred solution of triphenylphosphine (0.262 g, 1mmol) and 2,4-dimethyl-3-acetyl pyrrole (0.137 g, 1 mmol) in 5 mL of ethyl acetate was added, dropwise a solution of dialkyl acetylendicarboxylate(1 mmol) in 1 mL of ethyl acetate at -5°C over 10 min. The reaction mixture was allowed to warm up to room temperature and stirred for 1 hour. 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)-3-(triphenylphosphoranylidene)-butanedioate (3a)

The product of 3a (Z), was obtained as pale orange powder, m.p. 146-148°C, and yield 95%. IR (υ_{max}, cm^{-1}): 1735 (C=O of acetyl), 1730 (C=O of esters), 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 (300.1 MHz, $CDCl_3$): δ_H 1.41 (3H, s, CH_3), 2.05 (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 (75.47 MHz, $CDCl_3$): δ_c 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 (121.5 MHz, $CDCl_3$): δ_P 24.2 (s, Ph_3P^+-C).

Minor isomer, *E*-3a, (40%)

^{1}H NMR (300.1 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 (75.47 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 (121.5 MHz, $CDCl_3$): δ_P 24.9 (s, Ph_3P^+- C).

Diethyl 2-(2,4-dimethyl-3-acetyl pyrrole)-3-(triphenylphosphoranylidene)-butanedioate (3b) The product of ***Z*-3b**, was obtained as pale orange powder, m.p. 134-136°C, and yield 80%. IR (υ_{max}, cm^{-1}): 1735 (C=O of acetyl), 1730 (C=O of esteres), 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 (300.1 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 (75.47 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 (121.5 MHz, $CDCl_3$): δ_P 25.17 (s, Ph_3P^+- C).

Minor isomer (*E*-3b), (45%)
^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H ^{1}H NMR (300.1 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 (75.47 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 (121.5 MHz, $CDCl_3$): δ_P 25.0 (s, Ph_3P^+- C).

Di-tert-buthyl 2-(2,4-dimethyl-3-acetyl pyrrole)-3- (triphenylphosphoranylidene)-butanedioate (3c)
The product (Z)-3c was obtained as pale white powder, m.p. 160-162°C, and yield 90%. IR (υ_{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-$2CO_2{}^{t}Bu$, 5), 332 (M-$CO_2{}^{t}Bu$-($C_8H_{10}ON$-), 25), 287 (M-$2CO_2{}^{t}Bu$-($C_8H_{10}ON$-, 30), 77 (Ph, 8), 57 (^{t}Bu, 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 (300.1 MHz, $CDCl_3$): δ_H 0.9 (9H, s, ^{t}Bu), 1.54 (9H, s, ^{t}Bu), 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 (75.47 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, 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, $^{2}J_{PC}$=12.4 Hz, C=O), 170.2 (d, $^{3}J_{PC}$=13.1 Hz, C=O), 195.8 (s, C=O of $^{2}J_{PC}$=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}), acetyl). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 23.7 (s, Ph_3P^+- C).

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 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 most important geometrical parameters and also relative energies of both isomers.

Calculations

Structure and Stabilities
In order to determine more stable form of both ***Z*-3(a, c)** and ***E*-3(a, c)** isomer of ylides (3a and 3c), first their structures were optimized at HF/6-31G level of theory [30] by Gaussian 98 program package [31]. Also relative energies of the two isomers has been calculated at HF/6-31G and B3LYP/6-311++G (d,p) levels (See Figures 3 and 4). The relative stabilization energies for both ***Z*-3(a,c)** and ***E*-3(a,c)** isomers are reported in Table 1. As can be seen, ***Z*-3a** and ***Z*-3c** isomers are more stable than E-3a and E-3c forms (0.67, 3.08, 0.91 and 1.22 kcal/mol, respectively) at HF/6-31G and B3LYP/6-311++G(d,p) levels.

Table1: 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	1.22

Further investigation was undertaken in order to determine more effective factors on stability of both isomers, on the basis of AIM calculations [32] at HF/6-31G level of theory by the AIM2000 program package [33]. As noted in literature [34], the ranges of ρ(r) and $\nabla^2\rho(r)$ are 0.002-0.035e/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 *Z* and *E* isomers it is difficult to make a precise decision for determination of more stable isomer.

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

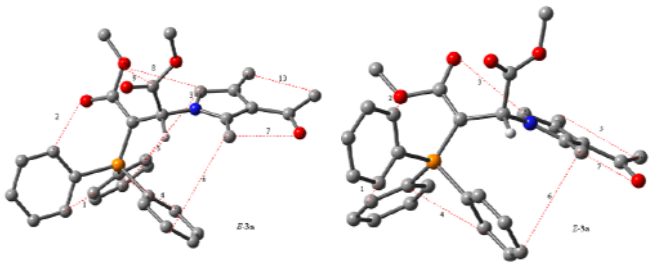
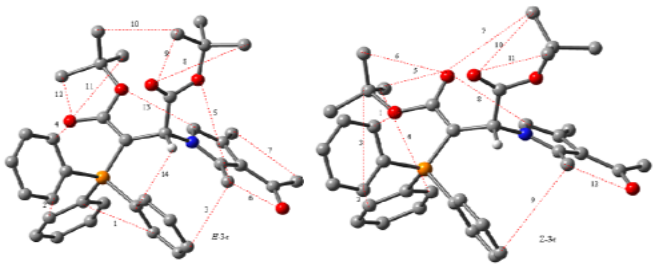


Figure 4: Intramolecular hydrogen bonds (dotted lines) in both **E-3a** and **Z-3a** isomers of stable ylides containing 2,4-dimethyl-3-acetyl pyrrole.



On the basis of theoretical calculations (Table 1), 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** (1.22 kcal/mol). Perhaps this noticeable difference is taken more in solution media for **3c**, for this reason it is possible to observe only one isomer of **3c** (*E* or *Z*). In experimental section both the ^{1}H NMR and ^{13}C NMR spectroscopies were indicated only one isomer for the **3c** ylide. Nevertheless, the result is different for **3a** (observed as the two isomers) which may be attributed to the negligible difference in relative stability of ***E*-3a** and ***Z*-3a** isomers. Perhaps this negligible difference (0.67 or 0.91 kcal/mol) is not taken more considerably in solution media for **3c**, for this reason, it is possible to see the two isomers of **3a** (both Z and E isomers). In recent case, the ^{1}H, ^{13}C, ^{31}P NMR data exhibited the two isomers of ylide **3a** which consistent with the obtained result from the theoretical investigations.

Conclusion

In conclusion, we have prepared a novel stable phosphorus ylides using a one-pot reaction between triphenylphosphine and acetylenic compounds in the presence of 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 a major or minor form in both of **3a** and **3c** ylides were undertaken by the theoretical study.

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