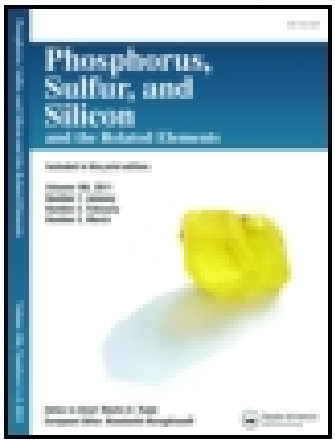

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# Synthesis of stable carbamate phosphorus ylides by a four-component reaction, and dynamic $^1$h nmr study of the energy barriers for the rotation around the carbon-nitrogen single bond and the carbon-carbon double bond

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# SYNTHESIS OF STABLE CARBAMATE PHOSPHORUS YLIDES BY A FOUR-COMPONENT REACTION, AND DYNAMIC $^1$H NMR STUDY OF THE ENERGY BARRIERS FOR THE ROTATION AROUND THE CARBON-NITROGEN SINGLE BOND AND THE CARBON-CARBON DOUBLE BOND

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**Abstract** A stable phosphorus ylide is obtained in high yield by a four component reaction between triphenylphosphine and dimethyl acetylendicarboxylate in the presence of the intermediate product formed from phenyl isocyanate and substituted phenols in dichloromethane at room temperature. This stable phosphorus ylide exists in solution as a mixture of two geometrical isomers resulting from restricted rotation around the carbon-carbon partial double bond due to conjugation of the ylide moiety with the adjacent carbonyl group. Dynamic effects are observed in $^1$H NMR spectra that are attributed to restricted rotation around the carbon-carbon double bond and the carbon-nitrogen single bond. These effects are used to calculate the free activation energy ($\Delta G^{\ddagger}$) and other activation parameters such as $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $E_a$.

**Keywords:** Dynamic $^{1}$H NMR; Free activation energy; Phosphorus ylide; Rotational energy barrier

## INTRODUCTION

The design of new synthetic routes and their development for widely used organic compounds from readily available reagents are the major tasks for an organic chemist.[1] Some reagents such as phosphorus ylides are important in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activities.[2] Phosphorus ylides are most often prepared by treatment of a phosphonium salts with a base. The phosphonium salts are usually made from the corresponding phosphine and an alkyl halide.[3-8] In addition, they are also obtained by Michael addition of phosphorus nucleophiles to activated oleýns.[3-11] Herein, we describe an efficient synthetic route for the synthesis of stable phosphorus ylides using triphenylphosphine (**4**), dimethyl acetylenedicarboxylate (**5**) and carbamates (**3**) in a four-component reaction. The synthesized phosphorus ylide exhibits dynamic $^{1}$HNMR effects that afford good information regarding the interchangeable process of rotational isomers that provide important kinetic data.[12-17]

## RESULTS AND DISCUSSION

Firstly, the work reports the reaction in which phenols (**1**) and phenyl isocyanate (**2**) lead to carbamates (**3**) that they can be utilized as NH source in the presence of triphenylphosphine (**4**) and dimethyl acetylenedicarboxylate **5** for the synthesis of dimethyl 2-[*N*-(4-

methylphenyl)phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene)butanedioates (**6**) in excellent yield. No other product could be detected by NMR spectroscopy. (Scheme 1)

**<Scheme 1>**

The structures of compounds **6a-e** were deduced from elemental analyses, IR, $^{1}H$, $^{31}P$, $^{13}C$ NMR and mass spectroscopy. The mass spectra displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve partial or complete loss of the side chains and scission of the aromatic rings. The $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra of the ylides **6a-e** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond of the (*E*)-**6** and (*Z*)-**6** geometrical isomers (Scheme 2) is slow on the NMR time scale at ambient temperature. Selected $^{1}H$, $^{13}C$ and $^{31}P$ NMR chemical shifts and coupling constants in the major and minor geometrical isomers of compound **6a-e** are shown in the experimental section. It must be mentioned that in compounds (**6a-e**) the *E*- and *Z*- geometrical isomers exist as major and minor isomers.

**<Scheme 2>**

The $^{1}H$ NMR spectrum of **6a** exhibited sharp singlet lines arising from methyl (ŭ = 2.28) and methoxycarbonyl groups (ŭ = 2.92 and 3.84) and a doublet from a methine proton (ŭ = 5.04, $^{3}J_{PH}$ = 20.0 Hz), respectively. All aromatic protons of **6a** resonated at ŭ = 7.03-7.73 for the major diasteroisomer.

The $^{13}C$ NMR spectrum of **6a** showed signals at ŭ = 153.86 and 168.62, $^{3}J_{PC}$ = 13.1 Hz and ŭ = 173.24, $^{2}J_{PC}$ = 15.9 Hz for carbamate and methoxy carbonyl groups, respectively. In addition, the observation of two signals in the $^{31}P$ NMR spectrum at ŭ = 24.06 and 24.78 indicates the existence of major and minor isomers. Other partial spectroscopic information is reported in the experimental section for the minor diasteroisomer.

Although the mechanism of this reaction has not been experimentally established, a proposed mechanism for this reaction is shown on the base of the literature [5-11, 18-23] in Scheme 3.

**<Scheme 3>**

Dynamic effects are observed in the $^{1}H$ NMR spectrum of **6a** at ambient temperature which has been attributed to the restricted rotational process around the partial carbon-carbon double bond, the carbon-carbon and the carbon-nitrogen single bonds[12,13] (see Schemes 4 and 5).

Two sharp doublets (ŭ = 5.04 and 5.06) are observed for the CH protons of the major and minor isomers of **6a** in the $^{1}H$ NMR spectrum in $CDCl_3$ as solvent at ambient temperature which appeared as a broad doublet at near to 55°C (328 K). An increasing of the temperature results in coalescence of the CH resonances. Recently, the free activation energy calculation using the expression $k = \acute{}\,q/\tilde{a}2$ the first order rate constant ($k_c$) for carbon-carbon double bond rotation has been reported by Shaabani et al.[24] Some spectroscopic data from this article have been extracted and collected in Table 1. From the coalescence temperature of the proton resonances of the CH group and by use of the equation for the rate constant, the first-order rate constant $k$ was

calculated for the bond rotation in **6a** to 24.53 $s^{-1}$ at 59°C. For this process, the activation and kinetic parameters involving $k_c$ and $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $E_a$ are summarized in Table 1.[26,27]

**<Scheme 4>**

**<Table 1>**

**<Table 2>**

**<Table 3>**

**<Scheme 5>**

**<Table 4>**

By further investigations and zooming in to $^1$H NMR spectra of **6a** another dynamic $^1$H NMR effect was observed which is attributed to the restricted rotational process around the carbonï nitrogen single bond.

When the temperature was decreased below ambient temperature, the $^1$H NMR spectrum of the major **6a**-isomer in $CDCl_3$ at +5°C showed a resonance arising from the methoxy protons which is broadened in comparison to a corresponding doublet measured at ambient temperature. When the temperature was further increased, the methoxy protons coalesce near 23°C (296 K) and appear as a sharp symmetrical resonance at 25°C, which is related to a restricted rotation around the carbon-nitrogen single bond in the major isomer of **6a** (see Scheme 2). It must be mentioned that the methoxy protons of the minor **6a**-isomer show coalescence near 20°C (293 K) and appear as a sharp symmetrical resonance at 25°C. These values are collected in Table 2.

The effect of temperature on the rate constant was investigated on the basis of measurement of different chemical shifts in a series of other separate experiments. The results were too small so that the changes in first-order rate constant and Gibbs free energy barrier are negligible in comparison with the results obtained at 23°C (296 K).[25]

The $^{1}$H NMR spectrum of **6a** in acetone at 0°C showed a resonance arising from the methoxycarbonyl protons that is appreciably broadened in comparison with a corresponding peak measured at ambient temperature (ŭ = 3.82), whereas the other signals remain unchanged. The methoxycarbonyl protons coalescence near –3°C and appear as fairly symmetrical resonance at –10°C, which is relevant to the restricted rotational around the carbon-carbon single bond (see Scheme 4 and Table 2).

More investigations are made for the restricted rotation around the nitrogen-carbon single bonds and results are summarized in Tables 3 and 4. An illustrative progress has been shown in Scheme 5.

## CONCLUSION

In conclusion, the novel four-component reaction between triphenylphosphine and dimethyl acetylenedicarboxylate in the presence of substituted phenols and phenyl isocyanate provides a simple, one-pot, and efficient route for the synthesis of stable, phosphorus ylides with probable pharmacological properties. The present procedure carries the advantage which allows us to calculate free activation energies qpG$^{ÿ}$.

## EXPERIMENTAL


ACCEPTED MANUSCRIPT

Melting points and IR spectra (KBr pellets, $\nu$/cm$^{-1}$) of all compounds were measured on an Electrothermal 9100 apparatus and a JASCO FT-IR spectrometer, respectively. The $^{1}$H, $^{13}$C, and $^{31}$P NMR spectra for compounds **6b-e** were obtained with a Bruker DRX-400 Avance instrument using $CDCl_3$ and acetone-$d_6$ as solvents, TMS as internal standard at 400.1, 100.6, 161.9 MHz except for compound **6a**, the spectra of which were obtained on a DRX-500 Avance instrument using $CDCl_3$ as solvent and TMS as internal standard at 500.1, 125.8, 202.4 MHz. VT NMR spectra for compound **6a** were performed at −17, −10, −5, 0, +5, +10, +15, +20, +25, +30, +50 and +60°C. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on an Agilent Technologies 5973 mass spectrometer operating at an ionization potential of 70 eV. Dimethyl acetylenedicarboxylate, phenols, phenyl isocyanate and triphenylphosphine were purchased from Fluka and were used without further puriýcation.



### General procedure for the preparation of ylide (6a)

Magnetic stirring of a solution of *p*-cresol (0.108 g, 1 mmol) and phenyl isocyanate (0.119 g, 1 mmol) under solvent-free condition for 6 h led to the formation of carbamate **3**. To this solution, a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) in 10 mL of $CH_2Cl_2$, dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) was added drop-wise over a period of 10 min at room temperature. After approximately 24 h of stirring at room temperature, the product was filtered off and washed with cold diethyl ether (3×5 mL).


ACCEPTED MANUSCRIPT

**Dimethyl 2-[*N*-(4-methylphenyl)phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene)butanedioate (6a)**. Yield: 0.57 g (90%); Orange powder; m.p. 154-157°C; IR: 1745, 1708, 1649 (C=O); MS *m/z*: 632.5 [$M^+$+1, 5], 631.5 [$M^+$, 15], 600.4 [7], 559.4 [3], 405.3 [100], 277.4 [23]; Anal. Calcd. for $C_{38}H_{34}NO_6P$ (631.65): C, 72.26; H, 5.43; N, 2.22; Found: C, 72.40; H, 5.54; N, 2.30%. ***Major isomer*** (*Z*)-**6a** (58%): $^1$H NMR (500.1 MHz, $CDCl_3$): ŭ 2.29 (3H, s, ArC*H*$_3$), 2.93 and 3.84 (6H, 2s, 2 OC*H*$_3$), 5.04 (1H, d, $^3J_{PH}$ = 20.0 Hz, P=C-C*H*), 7.03-7.73 (24H, m, $Ph_3P$, NPh and OAr); $^{13}$C NMR (125.8 MHz, $CDCl_3$): ŭ 20.83 (s, Ar*C*H$_3$), 40.56 (d, $^1J_{PC}$ = 134.8 Hz, P=*C*), 52.32 and 52.61 (2s, 2 O*C*H$_3$), 62.51 (d, $^2J_{PC}$ = 14.0 Hz, P=C-*C*H), 126.36 (d, $^1J_{PC}$ = 91.5 Hz, $C_{ipso}$), 128.83 (d, $^3J_{PC}$ = 12.1 Hz, $C_{meta}$), 132.25 (d, $^4J_{PC}$ = 2.0 Hz, $C_{para}$), 133.80 (d, $^2J_{PC}$ = 9.1 Hz, $C_{ortho}$), 118.67, 121.17, 127.17, 127.82, 129.41, 131.16, 134.23 (7s, $C_{arom}$), 149.39 (s, C, OAr), 153.86 (s, $CO_{carbamat}$), 168.62 (d, $^3J_{PC}$ =13.1 Hz, C=O), 173.24 (d, $^2J_{PC}$ = 15.9 Hz, P-C=*C*); $^{31}$P NMR (202.4 MHz, $CDCl_3$): ŭ 24.78 [s, ($Ph_3P^+$-C)]. ***Minor isomer*** (*E*)-**6a** (42%): $^1$H NMR (500.1 MHz, $CDCl_3$): ŭ 1.62 (3H, s, ArC*H*$_3$), 3.14 and 3.92 (6H, 2s, 2 OC*H*$_3$), 5.06 (1H, d, $^3J_{PH}$ = 17.6 Hz, P=C-C*H*), 7.03-7.73 (24H, m, $Ph_3P$, NPh and OAr); $^{13}$C NMR (125.8 MHz, $CDCl_3$): ŭ 15.34 (s, Ar*C*H$_3$), 41.90 (d, $^1J_{PC}$ = 129.7 Hz, P=*C*), 48.95 and 49.55 (2s, 2 O*C*H$_3$), 65.90 (d, $^2J_{PC}$ = 12.4 Hz, P=C-*C*H), 126.97 (d, $^1J_{PC}$ = 108.7 Hz, $C_{ipso}$), 128.72 (d, $^3J_{PC}$ = 10.1 Hz, $C_{meta}$), 132.13 (d, $^4J_{PC}$ = 3.0 Hz, $C_{para}$), 133.60 (d, $^2J_{PC}$ = 10.1 Hz, $C_{ortho}$), 118.67, 121.66, 126.30, 128.52, 129.39, 129.92, 134.23 (7s, $C_{arom}$), 148.90 (s, C, ArO), 153.30 (s, $CO_{carbamat}$), 170.03 (d, $^3J_{PC}$ = 12.9 Hz, C=O), 173.42 (d, $^2J_{PC}$ =16.0 Hz, P-C=*C*); $^{31}$P NMR (202.4 MHz, $CDCl_3$): ŭ 24.06 [s, ($Ph_3P^+$-C)].

**Dimethyl 2-[*N*-(2-methylphenyl)-*N*-phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene)butanedioate (6b)**. Yield: 0.60 g (95%); Orange powder; m.p. 157-159°C; IR:

1746, 1714, 1648 (C=O); MS *m/z*: 632.5 [$M^+$+1, 3], 631.5 [$M^+$, 11], 600.4 [3], 559.4 [4], 405.3 [100], 277.4 [55]; Anal. Calcd. for $C_{38}H_{34}NO_6P$ (631.65): C, 72.26; H, 5.43; N, 2.22; Found: C, 72.33; H, 5.48; N, 2.18%. ï ***Major isomer*** (*Z*)-**6b** (75%): $^1$H NMR (400.2 MHz, acetone-$d_6$): ŭ 2.10 (3H, s, ArC$H_3$), 2.91 and 3.91 (6H, 2s, 2 OC$H_3$), 5.01 (1H, d, $^3J_{PH}$ = 19.6 Hz, P=C-C*H*), 6.90-7.75 (24H, m, $Ph_3P$, NPh and OAr); $^{13}$C NMR (100.6 MHz, acetone-$d_6$): ŭ 22.11 (s, Ar*C*$H_3$), 41.29 (d, $^1J_{PC}$ = 136.8 Hz, P=*C*), 52.38 and 52.63 (2s, 2 O*C*$H_3$), 62.29 (P=C-*C*H, $^2J_{PC}$ = 17.0 Hz), 125.71 (d, $^1J_{PC}$ = 90.8 Hz, $C_{ipso}$), 128.95 (d, $^3J_{PC}$ = 12.8 Hz, $C_{meta}$), 132.29 (d, $^4J_{PC}$ = 2.3 Hz, $C_{para}$), 133.81 (d, $^2J_{PC}$ = 10.0 Hz, $C_{ortho}$), 118.70, 122.14, 127.15, 127.33, 128.60, 132.00, 134.51 (7s, $C_{arom}$), 145.69 (s, C, OAr), 152.30 (s, $CO_{carbamat}$), 170.13 (d, $^3J_{PC}$ =12.8 Hz, C=O), 173.02 (d, $^2J_{PC}$ = 14.1 Hz, P-C=*C*); $^{31}$P NMR (162.0 MHz, acetone-$d_6$): ŭ 24.11 [ s, ($Ph_3P^+$-C)], ï ***Minor isomer*** (*E*)-**6b** (25%): $^1$H NMR (400.2 MHz, acetone-$d_6$): ŭ 2.00 (3H, s, ArC$H_3$), 3.15 and 3.82 (6H, 2s, 2 OC$H_3$), 5.11 (1H, d, $^3J_{PH}$ = 19.4 Hz, P=C-C*H*), 6.90-7.75 (24H, m, $Ph_3P$, NPh and OAr); $^{13}$C NMR (100.6 MHz, acetone-$d_6$): ŭ 21.78 (s, Ar*C*$H_3$), 43.27 (d, $^1J_{PC}$ = 134.5 Hz, P=*C*), 48.62 and 49.46 (2s, 2 O*C*$H_3$), 63.27 (P=C-*C*H, $^2J_{PC}$ = 17.1 Hz), 125.52 (d, $^1J_{PC}$ = 91.0 Hz, $C_{ipso}$), 128.84 (d, $^3J_{PC}$ = 12.1 Hz, $C_{meta}$), 132.18 (d, $^4J_{PC}$ = 2.1 Hz, $C_{para}$), 133.58 (d, $^2J_{PC}$ = 10.1 Hz, $C_{ortho}$), 118.36, 122.43, 127.06, 127.70, 128.48, 132.00, 134.47 (7s, $C_{arom}$), 145.83 (s, C, OAr), 153.04 (s, $CO_{carbamat}$), 168.44 (d, $^3J_{PC}$ = 12.6 Hz, C=O), 171.68 (d, $^2J_{PC}$ = 13.8 Hz, P-C=*C*); $^{31}$P NMR (162.0 MHz, acetone-$d_6$): ŭ 24.71 [s, ($Ph_3P^+$-C)].

**Dimethyl 2-[*N*-(4-formylphenyl)-*N*-phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene)butanedioate (6c)**. Yield: 0.61 g (95%); Orange powder; m.p. 127-129°C; IR: 1745, 1712, 1644 (C=O); MS *m/z*: 646.5 [$M^+$+1, 4], 645.5 [$M^+$, 13], 614.3 [77], 587.6 [11], 467.5 [100]; Anal. Calcd. for $C_{38}H_{32}NO_7P$ (645.64): C, 70.69; H, 5.00; N, 2.17; Found: C, 70.47;

H, 5.13; N, 2.22%. ï ***Major isomer*** (*Z*)-**6c** (62%): $^{1}$H NMR (400.2 MHz, $CDCl_3$): ŭ 2.93 and 3.83 (6H, 2s, 2 OC*H*$_3$), 5.01 (1H, d, $^{3}J_{PH}$ = 20.1 Hz, P=C-C*H*), 7.12-7.81 (24H, m, $Ph_3P$, NPh and OAr), 9.94 (1H, s, ArC*H*O); $^{13}$C NMR (100.6 MHz, $CDCl_3$): ŭ 41.07 (d, $^{1}J_{PC}$ = 135.8 Hz, P=*C*), 52.43 and 52.71 (2s, 2 O*C*H$_3$), 61.97 (d, $^{2}J_{PC}$ = 16.0 Hz, P=C-*C*H), 121.87 (s, $C_{arom}$), 126.23 (d, $^{1}J_{PC}$ = 92.6 Hz, $C_{ipso}$), 128.87 (d, $^{3}J_{PC}$ = 12.1 Hz, $C_{meta}$), 132.35 (d, $^{4}J_{PC}$ = 1.9 Hz, $C_{para}$), 133.60 (d, $^{2}J_{PC}$ = 10.0 Hz, $C_{ortho}$), 126.92, 127.91, 129.95, 131.07, 133.02 (7s, $C_{arom}$), 138.27 (s, OAr), 152.63 (s, $CO_{carbamat}$), 168.61 (d, $^{3}J_{PC}$ = 13.3 Hz, C=O), 172.87 (d, $^{2}J_{PC}$ = 14.1 Hz, P-C=*C*), 191.12 (s, Ar*C*HO); $^{31}$P NMR (162.0 MHz, $CDCl_3$): ŭ 24.87 [s, ($Ph_3P^+$-C)]. ï ***Minor isomer*** (*E*)-**6c** (38%): $^{1}$H NMR (400.2 MHz, $CDCl_3$): ŭ 3.13 and 3.93 (6H, 2s, 2 OC*H*$_3$), 5.02 (1H, d, $^{3}J_{PH}$ = 19.5 Hz, P=C-C*H*), 7.12-7.81 (24H, m, $Ph_3P$, NPh and OAr), 9.94 (1H, s, ArC*H*O); $^{13}$C NMR (100.6 MHz, $CDCl_3$): ŭ 39.86 (d, $^{1}J_{PC}$ = 136.1 Hz, P=*C*), 49.55 and 48.98 (2s, 2 O*C*H$_3$), 62.79 (d, $^{2}J_{PC}$ = 17.1 Hz, P=C-*C*H), 122.19 (s, $C_{arom}$), 126.69 (d, $^{1}J_{PC}$ = 91.3 Hz, $C_{ipso}$), 128.72 (d, $^{3}J_{PC}$ = 12.3 Hz, $C_{meta}$), 132.11 (d, $^{4}J_{PC}$ = 2.0 Hz, $C_{para}$), 133.78 (d, $^{2}J_{PC}$ = 9.7 Hz, $C_{ortho}$), 127.09, 128.49, 129.42, 131.17, 133.44 (7s, $C_{arom}$), 138.57 (s, OAr), 151.84 (s, $CO_{carbamat}$), 169.88 (d, $^{3}J_{PC}$ =13.1 Hz, C=O), 173.25 (d, $^{2}J_{PC}$ =14.5 Hz, P-C=*C*), 191.12 (s, Ar*C*HO); $^{31}$P NMR (162.0 MHz, $CDCl_3$): ŭ 24.13 [s, ($Ph_3P^+$-C)].

**Dimethyl 2-[*N*-(2-Nitrophenyl)-*N*-phenylcarbamate-*N*-yl]-3-(triphenylphosphoranylidene)butanedioate (6d)**. Yield: 0.62 g (93%); Orange powder; m.p. 128-129°C; IR: 1746, 1714, 1645 (C=O), 1358 ($NO_2$); MS *m/z*: 663.5 [$M^+$+1, 2], 662.5 [$M^+$, 5], 631.5 [2], 407.4 [18], 405.3 [100], 335.3 [14], 277.4 [28]; Anal. Calcd. for $C_{37}H_{31}N_2O_8P$ (662.62): C, 67.07; H, 4.72; N, 4.23; Found: C, 67.16; H, 4.80; N, 4.15%. ï ***Major isomer*** (*E*)-**6d** (76%): $^{1}$H NMR (400.2 MHz, $CDCl_3$): ŭ 3.13 and 3.81 (6H, 2s, 2 OC*H*$_3$), 4.98 (1H, d, $^{3}J_{PH}$ = 20.0 Hz, P=C-C*H*),

7.10-8.10 (23H, m, $Ph_3P$, NPh and OAr); $^{13}C$ NMR (100.6 MHz, $CDCl_3$): ŭ 39.66 (d, $^1J_{PC}$ = 190.2 Hz, P=C), 52.38 and 52.61 (2s, 2 O*C*$H_3$), 62.32 (d, $^2J_{PC}$ = 17.1 Hz, P=C-*C*H), 126.71 (d, $^1J_{PC}$ = 88.5 Hz, $C_{ipso}$), 128.91 (d, $^3J_{PC}$ = 13.1 Hz, $C_{meta}$), 132.28 (d, $^4J_{PC}$ = 3.0 Hz, $C_{para}$), 133.8 (d, $^2J_{PC}$ = 10.1 Hz, $C_{ortho}$), 123.25, 126.60,127.54, 127.87, 130.00, 131.16 and 138.16 (7s, $C_{arom}$), 145.01 (s, OAr), 152.30 (s, $CO_{carbamat}$), 170.01 (d, $^3J_{PC}$ =18.1 Hz, C=O), 173.01 (d, $^2J_{PC}$ = 14.1 Hz, C=O); $^{31}P$ NMR (162.0 MHz, $CDCl_3$): ŭ 25.45 [s, ($Ph_3P^+$-C)]. ï ***Minor isomer*** (*Z*)-**6d** (24%): $^1H$ NMR (400.2 MHz, $CDCl_3$): ŭ 2.87, 3.89 (6H, 2s, 2 OC*H*$_3$), 5.01 (1H, d, $^3J_{PH}$ = 16.0 Hz, P=C-C*H*), 7.1-8.1 (23H, m, $Ph_3P$, NPh and OAr); $^{13}C$ NMR (100.6 MHz, $CDCl_3$): ŭ 40.98 (d, $^1J_{PC}$ = 199.2 Hz, P=C), 48.83 and 49.48 (2s, 2 O*C*$H_3$), 63.32 (d, $^2J_{PC}$ = 17.1 Hz, P=C-*C*H), 126.65 (d, $^1J_{PC}$ = 90.5 Hz, $C_{ipso}$), 128.84 (d, $^3J_{PC}$ = 12.1 Hz, $C_{meta}$), 132.17 (d, $^4J_{PC}$ = 3.0 Hz, $C_{para}$), 133.58 (d, $^2J_{PC}$ = 10.1 Hz, $C_{ortho}$), 123.25, 126.60, 127.54, 127.87, 129.95, 138.49 and 142.19 (7s, $C_{arom}$), 145.05 (s, OAr), 152.00 (s, $CO_{carbamat}$), 168.61 (d, $^2J_{PC}$ =13.1 Hz, C=O), 173.01 (d, $^3J_{PC}$ = 14.1 Hz, C=O); $^{31}P$ NMR (162.0 MHz, $CDCl_3$): ŭ 25.18 [s, ($Ph_3P^+$-C)].

**Dimethyl 2-[*N*-(2,6-dimethylphenyl)-*N*-phenylcarbamate-*N*-yl]-3-(triphenyl-phosphoranylidene)butanedioate (6e)**. Yield: 0.56 g (87%); Orange powder; m.p.: 184-187°C; IR: 1745, 1713, 1608 (C=O); MS *m/z*: 646.7 [$M^+$+1, 3], 645.6 [$M^+$, 5], 614.7 [8], 539.2 [14], 375.2 [100], 354.4 [19], 265.3 [13]; Anal. Calcd. for $C_{39}H_{36}NO_6P$ (645.68): C, 72.55; H, 5.62; N, 2.17; Found: C, 72.47; H, 5.64; N, 2.08%. ï ***Major isomer*** (*E*)-**6e** (69%): $^1H$ NMR (400.2 MHz, $CDCl_3$): ŭ 2.10 (6H, 2s, Ar*Me*$_2$), 3.18 and 3.83 (6H, 2s, 2 OC*H*$_3$), 5.02 (1H, d, $^3J_{PH}$ = 25.6 Hz, P=C-C*H*), 6.80-7.90 (23H, m, $Ph_3P$, NPh and OAr); $^{13}C$ NMR (100.6 MHz, $CDCl_3$): ŭ 16. 39 (s, Ar*Me*$_2$), 39.34 (d, $^1J_{PC}$ = 206.3 Hz, P=C), 49.54 and 52.29 (2s, 2 O*C*$H_3$), 61.50 (d, $^2J_{PC}$ = 17.1 Hz, P=C-*C*H), 126.34 (d, $^1J_{PC}$ = 92.6 Hz, $C_{ipso}$), 128.87 (d, $^3J_{PC}$ = 12.1 Hz, $C_{meta}$),

132.33 (d, $^{4}J_{PC}$ = 3.0 Hz, $C_{para}$), 133.78 (d, $^{2}J_{PC}$ = 10.1 Hz, $C_{ortho}$), 118.62, 125.14, 127.46, 128.14, 128.56, 131.39 and 139.05 (7s, $C_{arom}$), 148.74 (s, OAr), 152.84 (s, $CO_{carbamat}$), 170.17 (d, $^{3}J_{PC}$ = 18.1 Hz, C=O), 173.30 (d, $^{2}J_{PC}$ = 14.1 Hz, C=O); $^{31}$P NMR (162.0 MHz, $CDCl_3$): ŭ 24.78 [s, ($Ph_3P^+$-C)]. ï ***Minor isomer*** (*Z*)-**6e** (31%): $^{1}$H NMR (400.2 MHz, $CDCl_3$): ŭ 2.14 (6H, 2s, Ar*Me*$_2$), 2.90 and 3.89 (6H, 2s, 2 OC*H*$_3$), 5.00 (1H, d, $^{3}J_{PH}$ = 20.1 Hz, P=C-C*H*), 6.8-7.9 (23H, m, $Ph_3P$, NPh and OAr); $^{13}$C NMR (100.6 MHz, $CDCl_3$): ŭ 16. 39 (s, Ar*Me*$_2$), 40.65 (d, $^{1}J_{PC}$ = 215.3 Hz, P=C), 48.92 and 49.53 (2s, 2 O*C*H$_3$), 62.43 (d, $^{2}J_{PC}$ = 17.1 Hz, P=C-*C*H), 126.89 (d, $^{1}J_{PC}$ = 92.6 Hz, $C_{ipso}$), 128.76 (d, $^{3}J_{PC}$ = 12.1 Hz, $C_{meta}$), 132.20 (d, $^{4}J_{PC}$ = 2.0 Hz, $C_{para}$), 133.62 (d, $^{2}J_{PC}$ = 10.1 Hz, $C_{ortho}$), 121.75, 125.14, 126.85, 127.58, 128.54, 130.33, 139.36 (7s, $C_{arom}$), 148.74 (s, OAr), 152.50 (s, $CO_{carbamat}$), 168.67 (d, $^{3}J_{PC}$ = 13.1 Hz, C=O), 173.25 (d, $^{2}J_{PC}$ = 15.1 Hz, C=O); $^{31}$P NMR (162.0 MHz, $CDCl_3$): ŭ 24.27 [s, ($Ph_3P^+$-C)].

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**Table 1**. Selected $^{1}$H NMR chemical shifts δ/ppm of **6a** and **4a** (500 MHz) along with activation parameters in $CDCl_3$ for the restricted rotational process around the carbon-carbon double bond.

| **Compound** | Temp./°C | δ/ppm | Δν/Hz | $k_c/s^{-1}$ | $T_c/K$ | $\Delta G^{ÿ}$ kJmol$^{-1}$ | $\Delta H^{ÿ}$ kJmol$^{-1}$ | $\Delta S^{ÿ}$ kJmol$^{-1}$K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **6a** | 20 | 5.0198<br>5.0419 | 11.052 | 24.53 | 332 | 72.76±1 | | |
| | 60 | 5.06 | | | | | 59.241 | ï 0.0407 |
| | 20 | 6.7608<br>6.7991 | 19.155 | 42.53 | 330 | 70.79±1 | | |
| | 60 | 6.78 | | | | | | |
| **4a** | 25 | 4.83, 4.85 | 5.0 | 177.6 | 312 | 65.5[a] | | |
| **4a** | | **Major rotamer** | | | | | | |
| | $^{1}$H | 3.19 and 3.77 (6H, 2s, 2 $OCH_3$), 4.83 (1H, d, $^{3}J_{HP}$ 16.1 Hz, P-C-CH), 7.47ï 7.85 (19H, m, 3 $C_6H_5$ and $C_6H_4$). | | | | | | |
| | $^{13}$C | 37.35 (d, $^{1}J_{CP}$ 126.3 Hz, P=C), 49.78 and 53.56 (2s, 2 OMe), 55.76 (d, $^{2}J_{PC}$ 17.3 Hz P-C-CH), 123.37 (s, 2 CH, C $^{1}J_{PC}$ 92.0 Hz, $C_{ipso}$), 129.21 (d, $^{3}J_{PC}$ 12.3 Hz, $C_{meta}$), 132.44 (d, $^{4}J_{PC}$ 1 Hz, $C_{para}$), 132.75 (s, 2C, $C_6H_4$), 133.89 134.09 (d, $^{2}J_{PC}$ 10.0 Hz, $C_{ortho}$), 167.97 (2 C=O, phthalimide), 169.81 (d, $^{3}J_{PC}$ 14.0 Hz, C=O ester), 171.7 (d, $^{3}J$ ester). | | | | | | |
| | $^{31}$P | 23.84 (s, $Ph_3P$=C). | | | | | | |
| **4a** | | **Major rotamer** | | | | | | |
| | $^{1}$H | 3.66 and 3.73 (6H, 2s, 2 $OCH_3$). 4.85 (1H, d, $^{3}J_{HP}$ 17.5 Hz, P-C-CH), 7.47ï 7.85 (19H, m, 3 $C_6H_5$ and $C_6H_4$). | | | | | | |
| | $^{13}$C | 39.51 (d, $^{1}J_{CP}$ 131.0 Hz, P=C), 51.18 and 53.28 (2s, 2 OMe), 55.13 (d, $^{2}J_{PC}$ 17.3 Hz, P-C-CH), 123.36 (s, 2CH, $^{1}J_{PC}$ 92.3 Hz, $C_{ipso}$); 129.11 (d, $^{3}J_{PC}$ 12.3 Hz, $C_{meta}$), 132.45 (d, $^{4}J_{PC}$ 1.0 Hz, $C_{para}$), 132.65 (s, 2C, $C_6H_4$), 133.99 134.07 (d, $^{2}J_{PC}$ 6.5 Hz, $C_{ortho}$), 167.96 (2 C=O, phthalimide), 169.64 (d, $^{3}J_{PC}$ 13.7 Hz, C=O ester), 171.8 (d, $^{3}J_{I}$ ester). | | | | | | |
| | $^{31}$P | 24.00 (s, $Ph_3P$=C). | | | | | | |



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[a] Selected spectroscopic data and free activation energy for **4a** from ref. [24] are presented here.

**Table 2**. Selected $^{1}$H NMR chemical shifts δ/ppm of **6a** (500 MHz) along with activation parameters in $CDCl_3$ for the restricted rotational process around the carbon-carbon single bond in mode A and B (see Scheme 4).

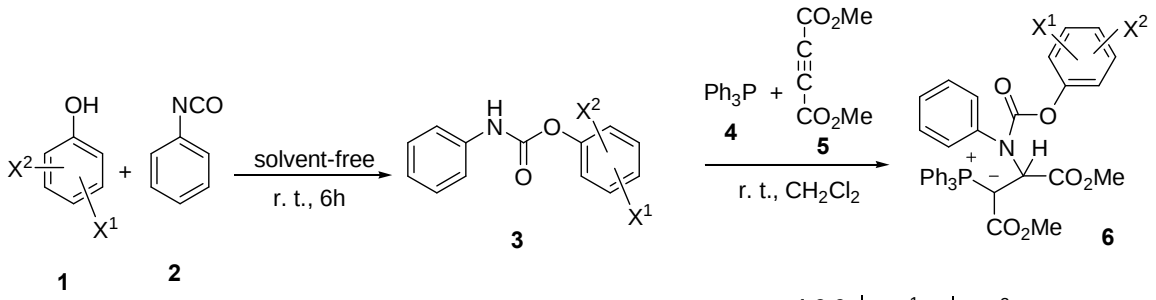
| **Compound** | Temp. °C | δ/ppm | Δν/Hz | $k_c/s^{-1}$ | $T_c/K$ | $\Delta G^{ÿ}$ $kJmol^{-1}$ | $\Delta H^{ÿ}$ $kJmol^{-1}$ | $\Delta S^{ÿ}$ $kJmol^{-1}K^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **6a-(major)** | 20 | 3.0947<br>3.2161 | 60.712 | 134.81 | 296 | 62.48±1 | | |
| | 50 | 3.14 | | | | | 48.12 | ï 0.044 |
| | 20 | 6.6595<br>6.7896 | 65.067 | 144.47 | 297 | 60.44±1 | | |
| | 50 | 6.79 | | | | | | |
| **6a-(minor)** | 20 | 3.8881<br>3.9351 | 23.606 | 52.19 | 293 | 61.83±1 | | |
| | 50 | 3.92 | | | | | 33.188 | ï 0.0985 |
| | 20 | 2.8904<br>2.9423 | 25.956 | 57.63 | 295 | 62.27±1 | | |
| | 50 | 6.79 | | | | | | |

**Table 3**. Selected $^1$H NMR chemical shifts δ/ppm of **6a** (500 MHz, $Me_4Si$) along with activation parameters $\Delta G^{\ddagger}$/kJmol$^{-1}$ in $CDCl_3$ for the restricted rotational process around the carbon-nitrogen single bonds in mode C and D (see Scheme 5).

| **Compound** | Temp/°C | δ/ppm $CO_2CH_3$ | Δν/Hz | $k_c$/s$^{-1}$ | $T_c$/K | $\Delta G^{\ddagger}$/kJmol$^{-1}$ |
|---|---|---|---|---|---|---|
| **6a-(major)** | 15 | 3.81, 3.84 | 15.00 | 33.32 | 270 | 58.00±2 |
| | 35 | 3.84 | | | | |
| **6a-(minor)** | 15 | 3.82, 3.85 | 15.00 | 33.32 | 254 | 54.43±2 |
| | 35 | 3.85 | | | | |

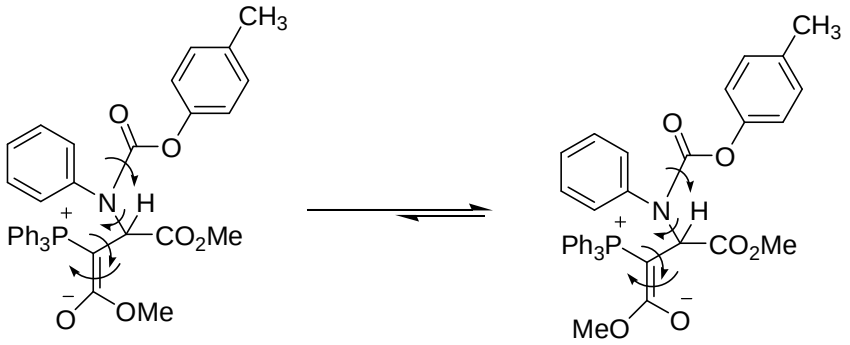
**Table 4**. Selected $^{1}H$ NMR chemical shifts δ/ppm of **6a** (500 MHz, $Me_4Si$) along with activation parameters in $CDCl_3$ for the restricted rotational process around the carbon-nitrogen single bonds in mode E and F (see Scheme 5).

| **Compound** | Temp./°C | δ/ppm $CO_2CH_3$ | qν/Hz | $k_c/s^{-1}$ | $T_c/K$ | qG$^{ÿ}$/kJmol$^{-1}$ |
|---|---|---|---|---|---|---|
| **6a-(major)** | ï 15 | 2.84, 2.85 | 5.00 | 11.10 | 294 | 64.11±2 |
| | 60 | 3.86 | | | | |
| **6a-(minor)** | ï 15 | 3.16, 3.18 | 10.00 | 21.81 | 296 | 62.88±2 |
| | 60 | 3.18 | | | | |



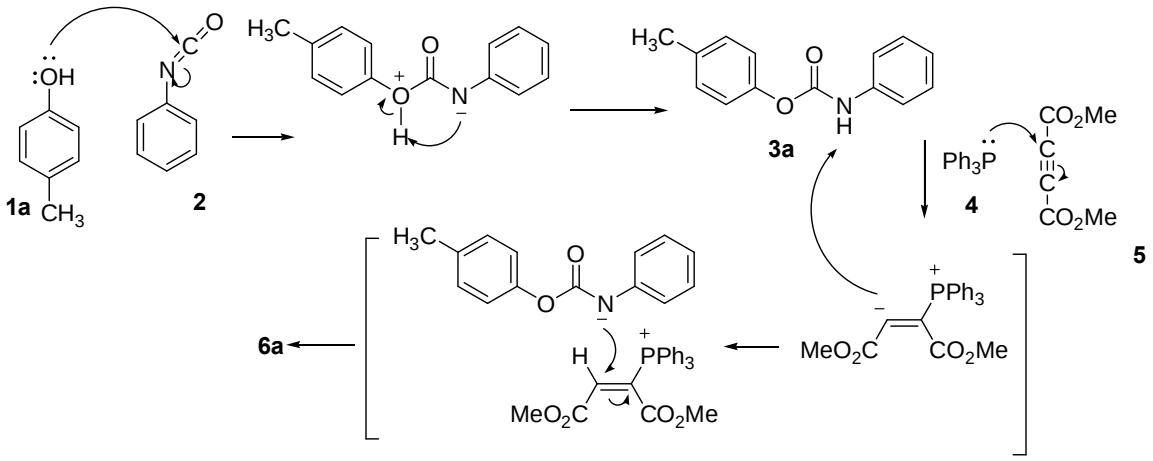

| 1,3,6 | $X^1$ | $X^2$ | % Yield |
|---|---|---|---|
| **a** | 4-Me | H | 90 |
| **b** | 2-Me | H | 93 |
| **c** | 4-CHO | H | 88 |
| **d** | 2-$NO_2$ | H | 93 |
| **e** | 2-Me | 6-Me | 87 |

**Scheme 1:** Synthesis of carbamate containing phosphorus ylides.

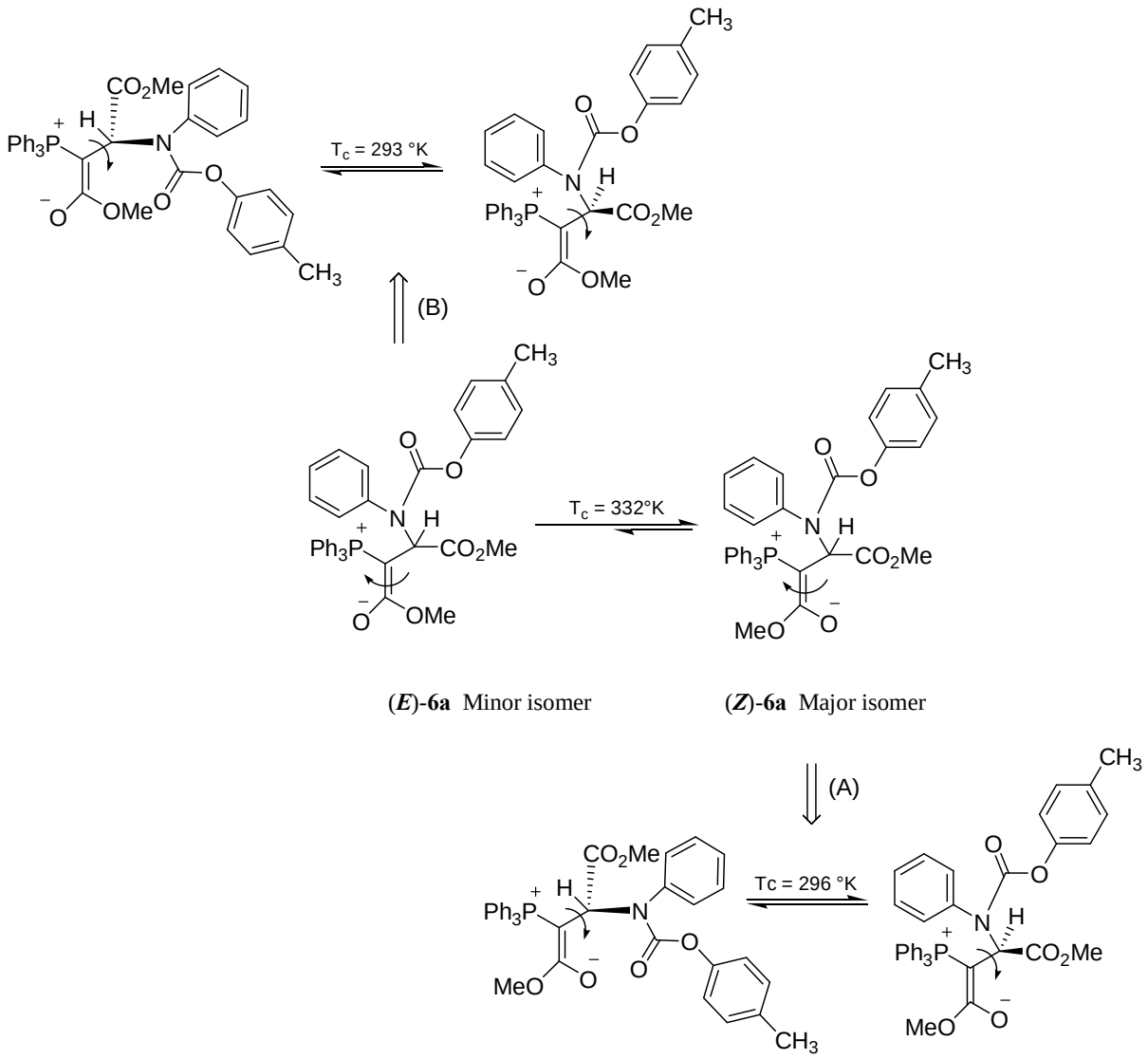



(***E***)-**6a** Minor isomer (***Z***)-**6a** Major isomer

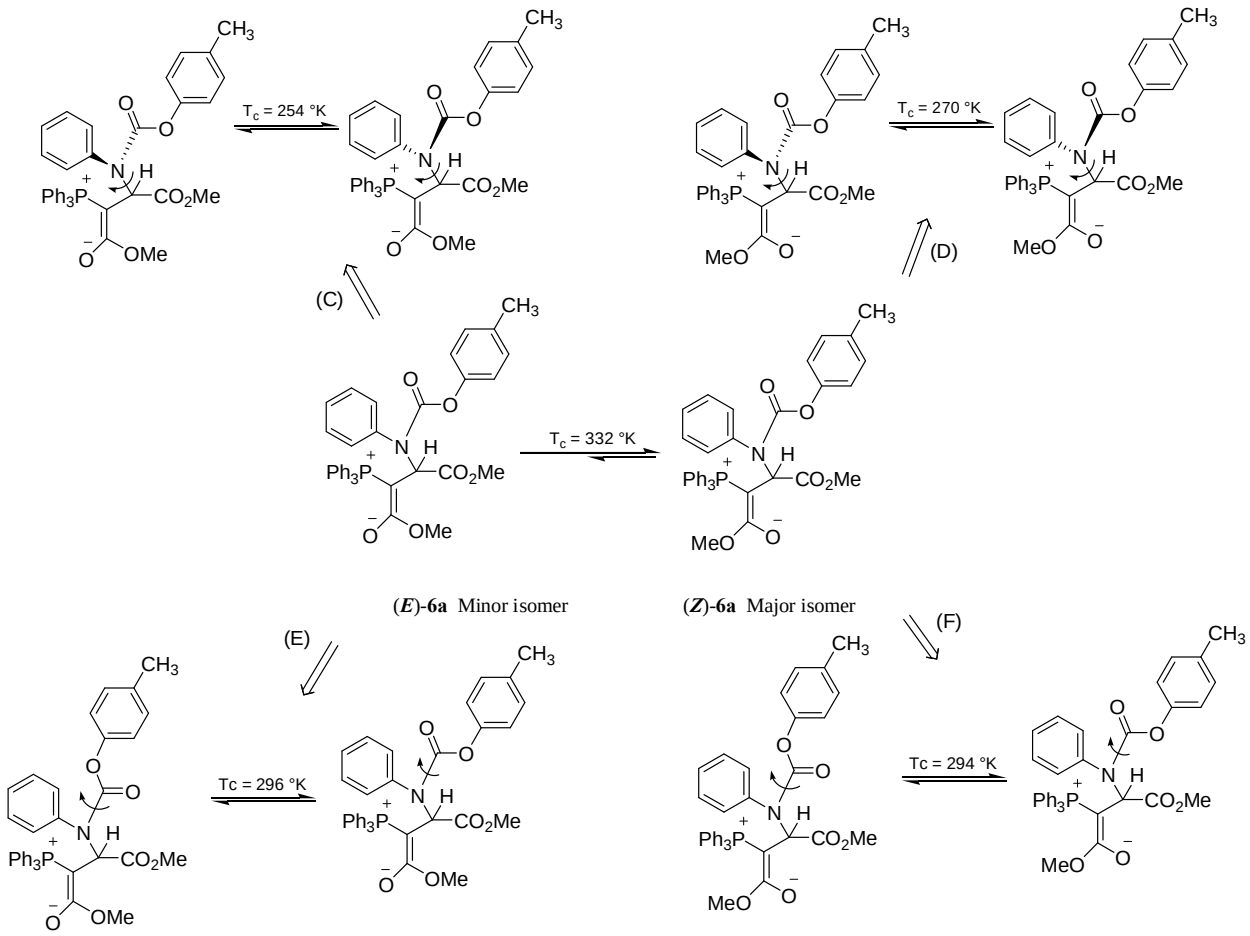
**Scheme 2:** *E* and *Z* geometrical isomers of phosphorus ylides as major and minor isomers.



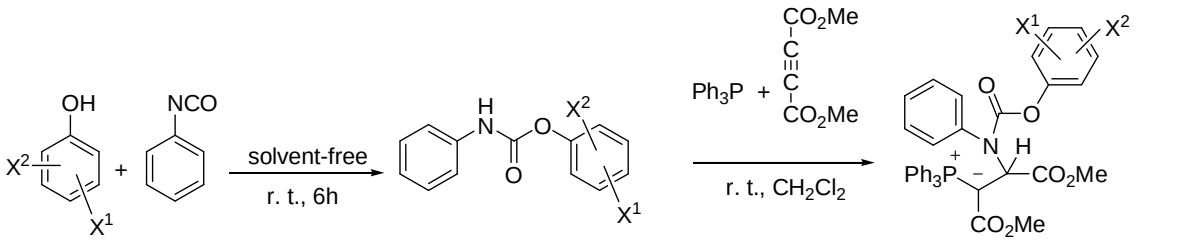

**Scheme 3:** A proposed mechanism for the synthesis of phosphorus ylides.




**Scheme 4:** Conformational interchanges around the C-C single bonds in the major and minor compounds.




**Scheme 5:** Conformational interchanges around the C-N single bond in the major and the minor diastereoisomers.




$X^1$: 2-Me, 4-Me, 4-CHO, 2-$NO_2$

$X^2$: H, 6-Me