Structural effects of different NH-acids and dialkyl acetylenedicarboxylates on the kinetic parameters of stable phosphorus ylids: a mechanistic investigation

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| C H R O N I C L E	A B S T R A C T
	Kinetic studies were made of the reactions between triphenylphosphine **1** and dialkyl acetylenedicarboxylates **2**, in the presence of NH-acids, such as benzotriazole, 5-methylbenzotriazole or 5-chlorobenzotriazole **3** (as a protic/nucleophilic reagent). To determine the kinetic parameters of the reactions, they were monitored by UV spectrophotometry. Useful information was obtained from studies of the effect of solvent, structure of reactants (dialkyl acetylenedicarboxylates and NH-acids) and also concentration of reactants on the reaction rates. First and third steps (k_2, k_3) of all reactions were recognized as a rate determining and fast steps, respectively. Proposed mechanism was confirmed on the basis of experimental data.

1. Introduction

Organophosphorus compounds have emerged as important reagents and intermediates in organic synthesis[1]. An important group of this class is phosphorus ylides, which have been used in many reactions and synthesis of organic compounds[2-29]. The prominent role of these compounds is to convert the carbonyl groups to carbon-carbon double bonds[7]. From the large number of methods available for the synthesis of phosphorus ylides, the most important one involves the reaction of a

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phosphonium salt with a base[14,20]. In recent years a method has been developed for the preparation of this family by using a novel approach employing vinyl phosphonium salts[15, 16]. The phosphonium salts are most often converted to the ylides by treatment with a strong base, though weaker bases can be used if the salt is acidic enough. Michael addition of phosphorus (III) compounds such as triphenylphosphine to acetylenic esters leads to reactive 1, 3-dipolar intermediate betaines which are not detected even at low temperatures[17]. These unstable species can be trapped by a protic reagent, ZH, such as methanol, amide, imide, *etc.* to produce various compounds *e.g.* ylides[5-29]. A facile reaction between triphenylphosphine **1**, dialkyl acetylenedicarboxilates **2** (**2d**, **2e** or **2f**) and imidazole, 2-methylimidazole or 4-methylimidazole **3** (**3a**, **3b** or **3c**) (as NH-acid) has been reported earlier[30], but the kinetic studies of this reaction has not been investigated yet. In order to gain further insight into the reaction mechanism, a kinetic study of the reaction between compounds **1**, **2** and **3** as NH-acid was undertaken by the UV spectrophotometeric technique. On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1-3] it is reasonable to assume that phosphorus ylide **4** results from the initial addition of triphenylphosphine to the acetylenic ester **2** (**2d**, **2e** or **2f**) (rate constant k_2) and subsequent protonation of the 1:1 adduct by the NH-acid **3** (**3a**, **3b** or **3c**) (rate constant k_3) to form phosphoranes **4** (rate constant k_4). To gain further insight into the reaction mechanism between triphenylphosphin **1,** dialkyl acetylenedicarboxylates **2** and **3** (**3a**, **3b** or **3c**) (as NH- heterocyclic compound) for generation of phosphorus ylides **4** (**Scheme 1**), a kinetic study of the reactions was undertaken by UV spectrophotometeric technique.

3, 4	a	b	c
Z			

4, 2	d	e	f
R	Me	Et	t-Bu

Scheme 1

2. Experimental

2.1. Chemicals and Apparatus Used

Dialkyl acetylenedicarboxylates, triphenylphosphine, benzotriazole, 5-methylbenzotriazole and 5-chlorobenzotriazole were purchased from Fluka (Buchs, Switzerland) and used without further purifications. All extra pure solvents including the 1,4-dioxan and 1,2-dichloroethane were obtained from Merck (Darmstadt, Germany). A Cary UV-Vis spectrophotometer model Bio-300 with a 10 mm light-path quartz spectrophotometer cell was employed throughout the current work.

2.2. Method

A first, it was necessary to find the appropriate wavelength to follow the kinetic study of the reaction. For this purpose, in the first experiment, 3×10^{-3} M solutions of compounds **1, 2f** and **3a** were prepared

in 1,4-dioxan. An approximately 3 mL aliquot from each reactant was pipetted into a 10 mm light path quartz spectrophotometer cell, and the relevant spectra were recorded over the wavelength range of 190-400 nm. **Figures 1**, **2** and **3** show the ultraviolet spectra of compounds **1**, **2f** and **3a** respectively. In a second experiment, a 1mL aliquot from the $3×10^{-3}$ M solutions of each compound of **1** and **3a** was pipetted first into a quartz spectrophotometer cell (as there is no reaction between them), later 1mL aliquot of the $3×10^{-3}$M solution of reactant **2f** was added to the mixture and the reaction monitored by recording scans of the entire spectra every 11 min at ambient temperature. The ultra-violet spectra shown in **Figure 4** are typical. From this, the appropriate wavelength was found to be 330 nm (corresponding mainly to product **4**), because at this wavelength, compounds **1**, **2f** and **3a** have relatively no absorbance value. This, then provided the opportunity to fully investigate the kinetics of the reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2f** and benzotriazole **3a** at 330 nm in the presence of 1, 2-dichloroethaneas solvent. Since the spectrophotometer cell of the UV instrument had a 10-mm light-path cuvette, the UV-Vis spectra of compound **4c** were measured over the concentration range ($2×10^{-4}$M $\le$ M$_{4c}$ $\le 10^{-3}$M) to check for a linear relationship between absorbance values and concentrations. With the suitable concentration range and wavelength identified, the following procedure was employed.
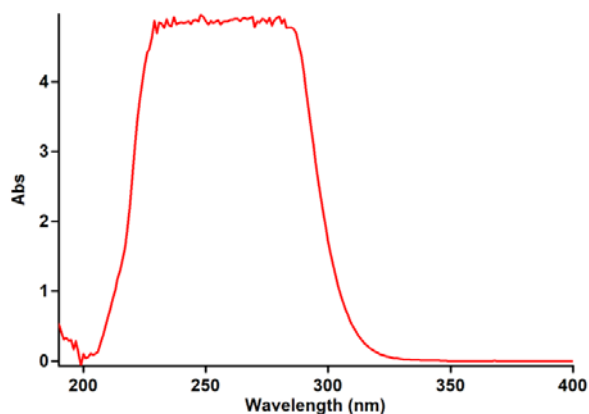
Fig. 1. The UV spectrum of 10^{-3} M triphenylphosphine **1** in 1,4-dioxan
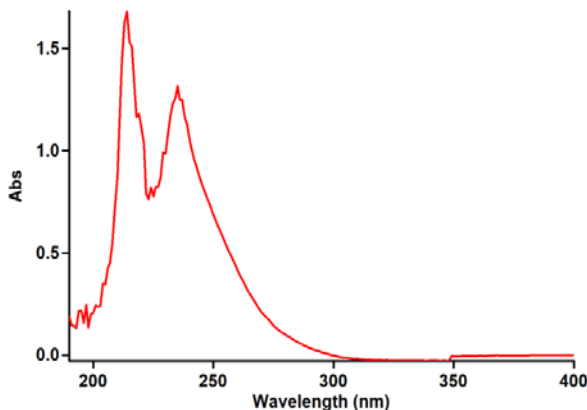
Fig. 2. The UV spectrum of 10^{-3} M di-*tert*-butyl acetylenedicarboxylate **2f** in 1,4-dioxan
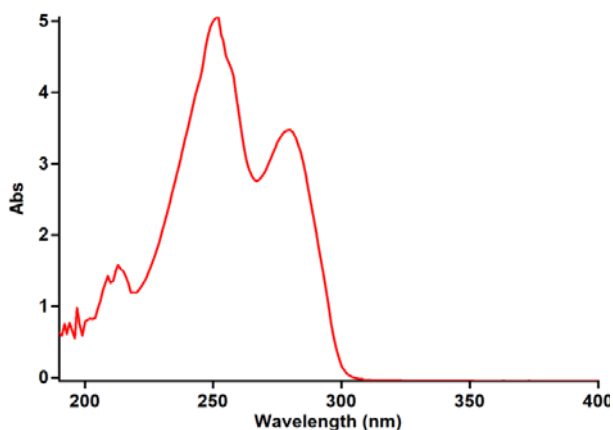

**Fig. 3**. The UV spectrum of 10^{-3} M benzotriazole **3a** in 1,4-dioxan
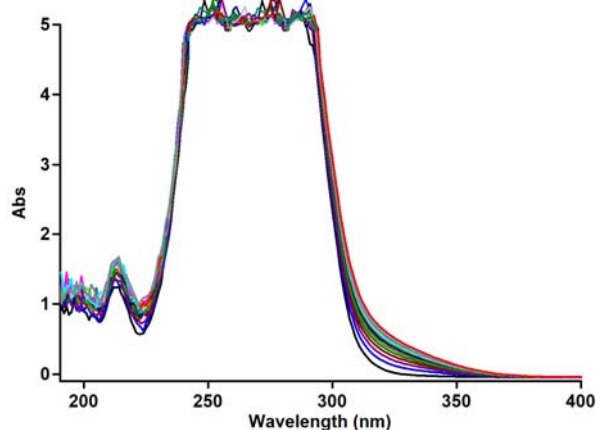
Fig. 4. The UV spectra of the reaction between 10^{-3} M of each compounds **1**, **2f** and **3a** as reaction proceeds in 1,4-dioxan

For each kinetic experiment, first a 1mL aliquot from each freshly made 3×10^{-3}M solution of compounds **1** and **3** in 1,4-dioxan was pipetted into a quartz cell, and then a 1mL aliquot of the 3×10^{-3}M of solution of reactant **2f** was added to the mixture, keeping the temperature constant at 12.0 ºC. The reaction kinetic was followed by plotting UV absorbance against time. **Figure 5** shows the absorbance change (dotted line) versus time for the 1:1:1 addition reaction between compounds **1**, **2f** and **3a** at 12.0 ºC. The infinity absorbance (A_∞) that is the absorbance at reaction completion, can be obtained from **Figure 5** at t =160 min. With respect to this value, zero, first or second curve fitting could be drawn automatically for the reaction by the software [31] associated with the UV instrument. Using the original experimental absorbance versus time data provided a second-order fit curve (full line) that fits exactly the experimental curve (dotted line) as shown in **Figure 6**. Thus, the reaction between triphenylphosphine **1**, di-*tert*-butyl acetylenedicarboxylate **2f** and **3a** follows second-order kinetics. The second-order rate constant (k_2) is then automatically calculated using a standard equation[31] within the program at 12.0 ºC. It is reported in Table **1**.
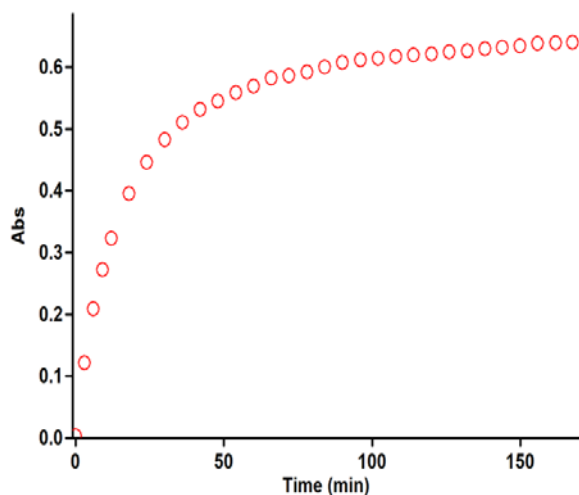
Fig. **5**. Experimental absorbance change (dotted line) against time at 330 nm for the reaction between compounds **1, 2f** and **3a** at 12.0 ºC in 1,4-dioxan
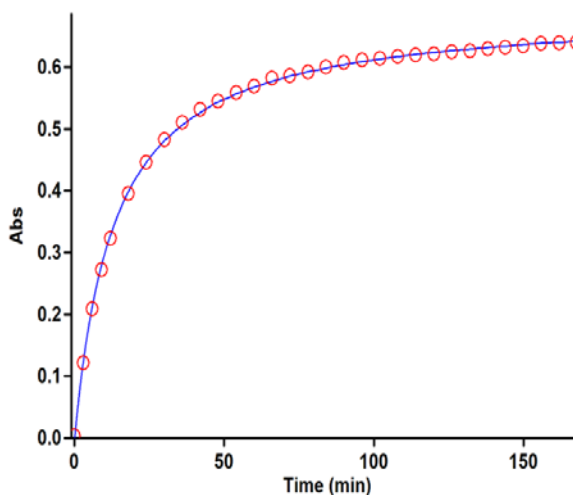
Fig. **6**. Second order fit curve (solid line) accompanied by the original experimental curve (dotted line) for the reaction between **1, 2f** and **3a** at 330 nm and 12.0 ºC in 1,4-dioxan

Furthermore, kinetic studies were carried out using the same concentration of each reactant in the continuation of experiments with concentrations of 5×10^{-3} M and 7×10^{-3} M respectively. As expected, the second-order rate constant was independent of concentration and its value was the same as in the previous experiment. In addition, the overall order of reaction was also 2.

2.3. Effect of solvents and temperature

To determine the effect of change in temperature and solvent environment on the rate of reaction, it was elected to perform various experiments at different temperatures and solvent polarities but otherwise under the same conditions as for the previous experiment. For this purpose, 1,2-dichloroethane with dielectric constant 10.3 respectively were chosen as a suitable solvent since it is not only could be dissolved all compounds but also did not react with them. The effects of solvents and temperature on the rate constant are given in Table **1**. The results show that the rate of reaction in each case was increased at higher temperature. In addition, the rate of reaction between **1**, **2f** and **3a** was accelerated in a higher dielectric constant environment (1,2-dichloroethane) in comparison with a lower dielectric constant environment (1,4-dioxan) at all temperatures investigated. In the temperature range studied, the dependence of the second-order rate constant ($\ln k_2$) of the reactions on reciprocal temperature is consistent with the Arrhenius equation.

Table 1 The values of second order rate constant for the three reactions (**1**, **2f** and **3a**), (**1**, **2f** and **3b**) and (**1**, **2f** and **3c**) in the presence of different solvents at all temperatures investigated

3	Solvent	ε	$k_2.M^{-1}.min^{-1}$			
			12.0 ºC	17.0 ºC	22.0 ºC	27.0 ºC
3a	1,4-dioxan	2.02	88.4	111.8	142.0	173.7
	1,2-dichloroethane	10.3	109.3	134.2	163.5	196.4
3b	1,4-dioxan	2.02	80.2	104.4	132.1	162.9
	1,2-dichloroethane	10.3	101.6	126.4	153.1	184.7
3c	1,4-dioxan	2.02	103.2	122.6	149.1	180.0
	1,2-dichloroethane	10.3	126.6	147.7	172.8	206.5

2.4. Effect of concentration

To determine reaction order with respect to triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2** (**2f**), in the continuation of experiments, all kinetic studies were carried out in the presence of excess **3**. Under this condition, the rate equation may therefore be expressed as:

$$rate = k_{obs}[1]^{\alpha}[2]^{\beta} \quad k_{obs} = k_2[3]^{\gamma} \quad \text{or} \quad \ln k_{obs} = \ln k_2 + \gamma \ln[3] \tag{1}$$

In this case (3×10^{-2} M of **3** instead of 3×10^{-3} M) using the original experimental absorbance versus time data provides a second order fit curve (full line) against time at 330 nm which exactly fits the experimental curve. The value of rate constant was the same as that of obtained from the previous experiment (3×10^{-3} M). Repetition of the experiments with 5×10^{-2}M and 7×10^{-2}M of **3** gave, separately, the same fit curve and rate constant. In fact, the experimental data indicated that the observed pseudo second order rate constant (k_{obs}) was equal to the second order rate constant (k_2), this is possible when γ is zero in equation (1). Therefore, It appears that the reaction is zero order with respect to **3** (protic/nucleophilic reagent) and second order with sum of **1** and **2** (**2f**) ($\alpha + \beta = 2$), respectively.

To determine reaction order with respect to dialkyl acetylenedicarboxylate **2** (**2f**), the continuation of experiment was performed in the presence of excess of **1** (rate $= k'_{obs}[3]^{\gamma}[2]^{\beta}$, $k'_{obs} = k_2 [1]^{\alpha}$ (2)). The original experimental absorbance versus time data and provide a pseudo first order fit curve at 330 nm, which exactly fits the experimental curve (dotted line) as shown in **Fig. 7**.
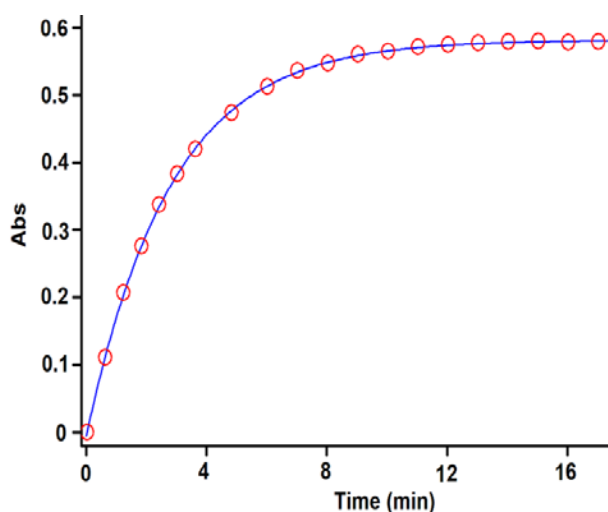
Fig. 7. Pseudo first order fit curve (solid line) for the reaction between **2f** and **3a** in the presence of excess **1** (10^{-2} M) at 330 nm and 12.0 ˚C in 1,4-dioxan.

As a result since $\gamma = 0$ (as determined previously), it is reasonable to accept that the reaction is first order with respect to compound **2** (**2f**) ($\beta = 1$). Because the overall order of reaction is 2 ($\alpha + \beta + \gamma = 2$) it is obvious that $\alpha = 1$ and order of triphenylphosphine **1** must be equal to one. This observation was obtained also for reactions between (**1**, **2e** and **3**) and (**1**, **2d** and **3**).

The experimental results indicate that the third step (rate constant k_3) is possibly fast. In contrast, it may be assumed that the third step is the rate determining step for the proposed mechanism. In this case the rate law can be expressed as follows:

$$rate = k_3 [I_1][3] \tag{3}$$

The steady state assumption can be employed for $[I_1]$ which is generated following equation,

$$[I_1] = \frac{k_2[1][2]}{k_{-2} + k_3[3]}$$

The value of $[I_1]$ can be replaced in equation (3) to obtain this Eq.

$$rate = \frac{k_2 k_3 [1][2][3]}{k_{-2} + k_3 [3]}$$

Since it was assumed that k_3 is relevant to the rate determining step, it is reasonable to make the following assumption:

$$k_{-2} \gg k_3 [3]$$

So the rate of low becomes:

$$rate = \frac{k_2 k_3 [1][2][3]}{k_{-2}}$$

The final equation is indicates that overall order of reaction is three which is not compatible with experimental overall order of reaction (= 2). In addition, according to this equation, the order of reaction with respect to NH-acid **3** is one, whereas it was actually shown to be equal to zero. For this reason, it appeared that the third step is fast. If we assume that the fourth step (rate constant k_4) is the rate-determining step for the proposed mechanism, in this case, there are two ionic species to consider in the rate determining step, namely phosphonium ion (I_2) and benzotriazole ion (Z^-). The phosphonium and benzotriazole ions, as we see in **Fig. 8**, have full positive and negative charges and form very powerful ion-dipole bonds to the 1,2-dichloroethane, the high dielectric constant solvent. However, the transition state for the reaction between two ions carries a dispersed charge, which here is divided between the attacking benzotriazole and the phosphonium ions. Bonding of solvent (1,2-dichloroethane) to this dispersed charge would be much weaker than to the concentrated charge of benzotriazole and phosphonium ions. The solvent thus stabilize the species ions more than it would the transition state, and therefore E_a would be higher, slowing down the reaction. However, in practice, 1,2-dichloroethane speeds up the reaction and for this reason, the fourth step, which is independent of the change in the solvent medium, could not be the rate determining step. Furthermore, the rate law of formation of the product (fourth step) for a proposed reaction mechanism with application of steady state assumption can be expressed by:

$$rate = k_4 [I_2] [Z^-]$$

By application of steady state for $[I_2]$ and $[Z^-]$, and replacement of their values in the above equation, the following equation is obtained:

$$rate = \frac{k_2 k_3 [1][2][3]}{k_{-2} + k_3 [3]} \qquad (4)$$

This equation is independent of rate constant for the fourth step (k_4) and shows why the fourth step would not be affected by a change in the solvent medium. In addition, it has been suggested earlier that the kinetics of ionic species phenomena (e.g., the fourth step) are very fast. If the first step (rate constant k_2) were the rate determining step, in this case, two reactants (triphenylphosphine **1** and dialkyl acetylenedicarboxylate **2**), as we see in **Fig. 8**, have no charge and could not form strong ion-dipole bonds to the high dielectric constant solvent, 1, 2-dichloroethane. However, the transition state carries a dispersed charge which here is divided between the attacking **1** and **2** and, hence, bonding of solvent to this dispersed charge is much stronger than the reactants, which lack charge. The solvent thus stabilizes the transition state more than it does the reactants and, therefore, E_a is reduced which speeds up the reaction. Our experimental results show that the solvent with higher dielectric constant exerts a power full effect on the rate of reaction (in fact, the first step has rate constant k_2 in the proposed mechanism) but the opposite occurs with the solvent of lower dielectric constant, (see Table **1**). The results of the current work (effects of solvent and concentration of compounds) have provided useful evidence for steps 1 (k_2), 3 (k_3) and 4 (k_4) of the reactions between triphenylphosphine **1**, dialkyl acetylenedicarboxylate **2** (**2d**, **2e** or **2f**) and NH-acid **3** (**3a**, **3b** or **3c**). Two steps involving 3 and 4 are not determining, although the discussed effects, taken altogether, are compatible with first step (k_2) of the proposed mechanism and would allow it to be the rate-determining step. However, a good kinetic description of the experimental result using a mechanistic scheme based upon the steady state approximation is frequently taken as evidence of its validity. By application of this, the rate formation of product **4** from the reaction mechanism (**Fig. 8**) is given by:

$$\frac{d[4]}{dt} = \frac{d[ylide]}{dt} = rate = k_4 [I_2][Z^-] \qquad (5)$$

We can apply the steady-state approximation to $[I_1]$ and $[I_2]$;

$$\frac{d[I_1]}{dt} = k_2 [1][2] - k_{-2}[I_1] - k_3 [I_1][3],$$

$$\frac{d[I_2]}{dt} = k_3 [I_1][3] - k_4 [I_2][Z^-]$$

To obtain a suitable expression for $[I_2]$ to put into equation (5) we can assume that, after an initial brief period, the concentration of $[I_1]$ and $[I_2]$ achieve a steady state with their rates of formation and rates of disappearance just balanced. Therefore $\dfrac{d[I_1]}{dt}$ and $\dfrac{d[I_2]}{dt}$ are zero and we can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

$$\frac{d[I_2]}{dt} = 0 \quad , \quad [I_2] = \frac{k_3 [I_1][3]}{k_4 [Z^-]} \qquad (6)$$

$$\frac{d[I_1]}{dt} = 0 \quad , \quad [I_1] = \frac{k_2 [1][2]}{k_{-2} + k_3 [3]} \qquad (7)$$

We can now replace $[I_1]$ in the Eq. (6) to obtain this equation:

$$[I_2] = \frac{k_2 k_3 [1][2][3]}{k_4 [Z^-][k_{-2} + k_3 [3]]}$$

The value of $[I_2]$ can be put into equation (5) to obtain the rate Eq. (8) for proposed mechanism:

$$rate = \frac{k_2 k_3 k_4 [1][2][3][Z^-]}{k_4 [Z^-][k_{-2} + k_3 [3]]} \qquad \text{or} \qquad rate = \frac{k_2 k_3 [1][2][3]}{[k_{-2} + k_3 [3]]} \qquad (8)$$

Since experimental data were indicated that steps 3 (k_3) and 4 (k_4) are fast but step 1 (k_2) is slow, it is therefore reasonable to make the following assumption:

$$k_3 [3] \gg k_{-2}$$

So the rate equation becomes:

$$rate = k_2 [1][2] \tag{9}$$

This equation which was obtained from a mechanistic scheme (shown in **Fig. 8**) by applying the steady-state approximation is compatible with the results obtained by UV spectrophotometery. With respect to the Eq. (9) that is overall reaction rate, the activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ could be now calculated for the first step (rate determining step), as an elementary reaction, on the basis of Eyring equation. The results are reported in Table **4**.
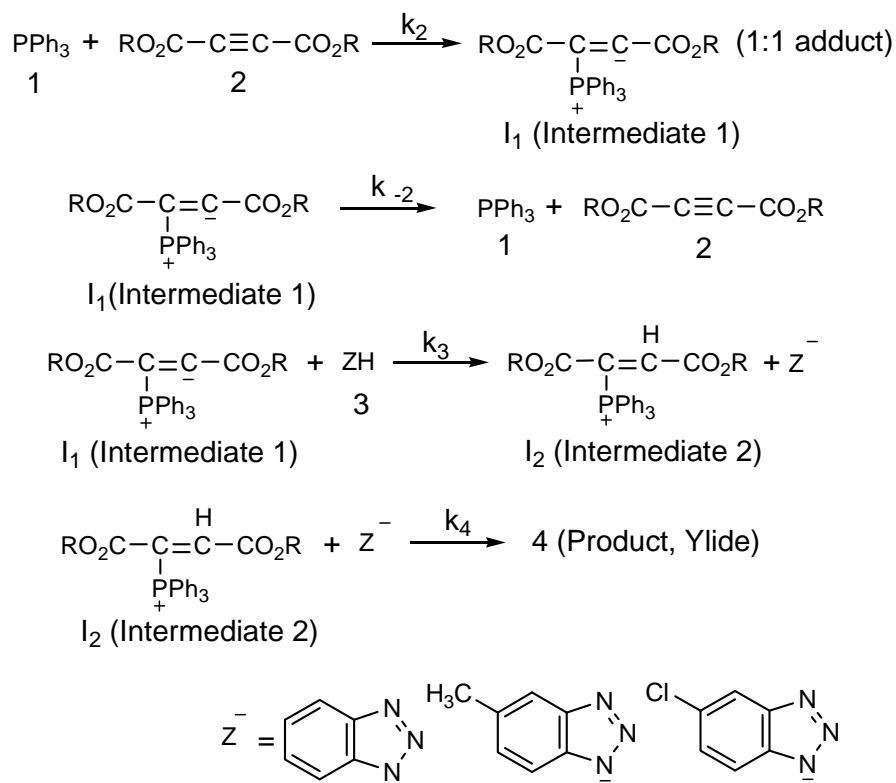
Fig. **8**. Mechanism proposed for the reaction between **1**, **2** (**2d**, **2e** or **2f**) and **3** (**3a**, **3b** or **3c**) on the basis of literatures for generation of phosphorus ylides **4**.

2.5. Further kinetic investigations

2.5.1. Effect of structure of dialkyl acetylenedicarboxylates

To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2e** and dimethyl acetylenedicarboxylate **2d**, respectively, under the same conditions used in the previous experiments. The values of the second-order rate constant (k_2) for the reactions between (**1**, **2e** and **3**) and (**1**, **2d** and **3**) are reported in Table **2**, for all solvents and temperatures investigated.

Table 2 The values of second order rate constant for the reaction between **1**, **2e** and **3** in the presence of different solvents at all temperatures investigated

3	Solvent	ε	$k_2.M^{-1}.min^{-1}$			
			12.0 ºC	17.0 ºC	22.0 ºC	27.0 ºC
3a	1,4-dioxan	2.02	377.2	418.6	492.1	612.4
	1,2-dichloroethane	10.3	521.4	653.0	854.1	1036.2
3b	1,4-dioxan	2.02	278.6	297.4	356.5	458.3
	1,2-dichloroethane	10.3	475.6	569.2	659.4	848.2
3c	1,4-dioxan	2.02	491.8	544.2	598.6	713.2
	1,2-dichloroethane	10.3	635.2	780.1	96.0	1163.5

Table 3 The values of second order rate constant for the reaction between **1**, **2d** and **3** in the presence of different solvents at all temperatures investigated

3	Solvent	ε	$k_2.M^{-1}.min^{-1}$			
			12.0 ºC	17.0 ºC	22.0 ºC	27.0 ºC
3a	1,4-dioxan	2.02	408.1	476.3	546.6	625.2
	1,2-dichloroethane	10.3	626.9	742.3	931.8	1191.6
3b	1,4-dioxan	2.02	381.7	431.3	502.1	599.7
	1,2-dichloroethane	10.3	531.2	623.1	721.0	851.4
3c	1,4-dioxan	2.02	577.0	621.1	687.9	783.8
	1,2-dichloroethane	10.3	712.5	855.1	1045.3	1295.7

Table 4 The activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ for the reactions between (**1**, **2f** and **3a)**, (**1**, **2f** and **3b)** and (**1**, **2f** and **3c)** in 1,4-dioxan

Reactions	Ea (kJ.mol^{-1})	$\Delta G^{\#}$ (kJ.mol^{-1})	$\Delta H^{\#}$ (kJ.mol^{-1})	$\Delta S^{\#}$ (J.mol^{-1}.K^{-1})
1, **2f** and **3a**	32.2	69.8	29.8	-136.7
1, **2f** and **3b**	33.6	70.0	31.2	-132.7
1, **2f** and **3c**	26.5	69.6	24.1	-155.6

As can be seen from Tables **2** and **3** the behavior of diethyl acetylenedicarboxylate **2e** and dimethyl acetylenedicarboxylate **2d** is the same as for the di-*tert*-butyl acetylenedicarboxylate **2f** with respect to the reaction with triphenylphosphine **1** and NH-acid **3** (**3a**, **3b** and **3c**). The rate of the former reactions was also accelerated in a higher dielectric constant environment and with higher temperatures; however, these rates under the same condition are approximately 4 to 7 times more than for the reaction with di-*tert*-butyl acetylenedicarboxylate **2f**. It seems that both inductive and steric factors for the bulky alkyl groups in **2f** tend to reduce the overall reaction rate (see equation **9**). In the case of dimetyl acetylenedicarboxylate **2d**, the lower steric and inductive effects of the dimethyl groups exert a powerful effect on the rate of reaction.

2.5.2. Effect of structure of NH-acids (substituted group on the ring of benzotriazole

Reproducible experiments were investigated in the presence of other NH-acids such as 5-methylbenzotriazole **3b** or 5-chlorobenzotriazole **3c** under the same conditions used in the previous experiments, the rate of reactions were reduced in comparison with benzotriazole **3a** respectively. It seems that the effect of electron donor of substituted methyl groups in position 5 of benzotriazole ring would tend to reduce the chemical activity of NH-acid, conversely electron withdrawal of halogen

group in the same position would tend to increase the chemical activity of NH-acid in comparison with benzotriazole **3a** (see Tables **1**, **2** and **3**). Practically, experimental data were indicate that change within the structure of NH-acid has no effect on the priority of the rate determining step of the reaction and step 1 (rate constant k_2) is still the rate determining step, in the presence of new NH-acids **3c** or **3b** and order of reaction with respect to them is still zero. Because of the chemical activity of NH-acid is dependent on its structure, this provide opportunity in order to change the rate constant k_3 (NH-acid participate in this step) and also subsequent alteration of overall rate constant of reaction (see equation 8).

3. Conclusions

Kinetic investigation of these reactions was undertaken using UV spectrophotometry. The results can be summarized as follow: (**1**) the appropriate wavelengths and concentrations were determined to follow the reaction kinetics. (**2**) The overall reaction order followed second-order kinetics and the reaction orders with respect to triphenylphosphine, dialkyl acetylenedicarboxylate and NH-acid were one, one and zero respectively. (**3**) The values of the second-order rate constants of all reactions were calculated automatically with respect to the standard equation, using the software associated with the Cary-300 UV equipment. (**4**) The rates of all reactions were accelerated at higher temperatures. Under the same conditions, the activation energy for the reaction in the presence of benzotriazole **3a** (32.2 kJ/mol) was higher than that for the both reactions which were followed by the 5-methylbenzotriazole **3b** (33.6 kJ/mol) and 5-chlorobenzotriazole **3c** (26.5 kJ/mol) in 1,4-dioxan (**5**) The rates of all reactions were increased in solvents of higher dielectric constant and this can be related to differences in stabilization by the solvent of the reactants and the activated complex in the transition state. (**6**) Increased steric bulk in the alkyl groups of the dialkyl acetylenedicarboxylates, accompanied by the correspondingly greater inductive effect, reduced the overall reaction rate. (**7**) With respect to the experimental data, the first step of proposed mechanism was recognized as a rate-determining step (k_2) and this was confirmed based upon the steady-state approximation. (8) Also, the third step was identified as a fast step (k_3). (9) The activation parameters involving $\Delta G^{\#}$, $\Delta S^{\#}$ and $\Delta H^{\#}$ were reported for three reactions.

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