A Facile Synthesis of Stable Phosphorus Ylides Derived from 3,6-Dibromocarbazole and Kinetic Investigation of the Reactions by UV Spectrophotometry Technique

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ABSTRACT: Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, in the presence of NH-acid, such as 3,6-dibromocarbazole. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carboncarbon partial double bond, resulting from the conjugation of the ylide moiety with the adjacent carbonyl group. To determine the kinetic parameters of the reactions, they were monitored by UV spectrophotometry. The second-order fits were drawn, and the values of the second-order rate constant (k_2) were calculated using standard equations within the program. At the temperature range studied, the dependence of the second-order rate constant ($\ln k_2$) on reciprocal temperature was in a good agreement with the Arrhenius equation. This provided the relevant plots to calculate the activation energy of all reactions. Furthermore, useful information was obtained from studies of the effect of solvent, structure of reactants (different alkyl groups within the dialkyl acetylenedicarboxylates), and also the concentration of reactants on the

rate of reactions. The proposed mechanism was confirmed according to the obtained results and a steadystate approximation and the first step (k_2) of reaction was recognized as a rate-determining step on the basis of the experimental data. © 2008 Wiley Periodicals, Inc. Heteroatom Chem 19:723–732, 2008; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20501

INTRODUCTION

Development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic chemistry [1]. Phosphorus ylides are reactive systems, which take part in many valuable reactions of the organic synthesis [2–11], and they are most often prepared by the treatment of a phosphonium salt with a base. Most of the phosphonium salts are prepared from the reaction of phosphine and an alkyl halide [3–7], though they can be obtained also by the Michael addition of phosphorus nucleophiles to activated olefins [2,3]. Herein, we describe an efficient synthetic route to, and kinetic study of, stable phosphorus ylides, using triphenylphosphine, dialkyl acetylenedicarboxylates, and NH-acid such as 3,6-dibromocarbazole. As noted earlier, the carbazole moiety and its derivatives are widely used in

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FIGURE 1 The reaction between triphenylphosphine 1, dialkyl acetylenedicarboxylate 2 (2a, 2b, or 2c), and 3,6dibromocarbazole 3 for generation of stable phosphorus ylides 4(4a, 4b, or 4c).

the preparation of medicines [12]. With respect to the importance of the recent purposes, the present work was undertaken for the generation of stable phosphoranes. Accordingly, the reaction of triphenylphosphine 1 with dialkyl acetylenedicarboxylates 2 (2a, 2b, or 2c) in the presence of a NH-acid 3 led to the corresponding stable heterocyclic phosphorus ylides 4 (4a, 4b, or 4c) in excellent yields (see Fig. 1).

RESULTS AND DISCUSSION

Reactions of 3,6-dibromocarbazole **3** with dialkyl acetylenedicarboxylates **2** in the presence of triphenylphosphine **1** were carried out in acetone at room temperature and were completed within a few hours. The ¹H and ¹³C NMR spectra of the crude products clearly indicated the formation of stable phosphorus ylides **4**. Any products other than **4** could not be detected by NMR spectroscopy. The structures of compounds **4a–c** were deduced from their IR, ¹H,



FIGURE 2 Two geometrical isomers (major and minor) of stable phosphorus ylides 4 (4a or 4b).

¹³C, and ³¹P NMR spectra. Their mass spectra displayed molecular ion peaks at appropriate m/z values, and initial fragmentations involve the loss of parts or complete side chains and scission of the heterocyclic ring system. The ¹H, ¹³C, and ³¹P NMR spectra of ylides 4a and 4b are consistent with the presence of two isomers. The ylides moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and rotation around the partial double bond in (E)-4 and (Z)-4 geometrical isomers is slow on the NMR time scale at ambient temperature (see Fig. 2). Selected ¹H, ¹³C, and ³¹P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds 4a and 4b are presented in Table 1. As can be observed, only one geometrical isomer (Z)-4 was observed for 4c, presumably, because of the bulky tertbutyl groups.

The structural assignment of (E)-4 and (Z)-4 rotamers as the major or minor form in phosphorus ylides has been previously established and is reported in the literature [13–16]. Herein, the ¹H NMR



Br Ha Ha Br	Br Ha Ha Br
*/ `0 PhgP (<i>E</i>)-4: Minor	PhaP OR (Z)-4; Major

Compound R in 4		¹ H NMR Spectroscopy Data						
	Isomer (%)	H-2 (³ J _{PH})	OR	CO_2R	C-2 (² J _{PC})	C-3 (¹ J _{PC})	³¹ P NMR	
4a	Ме	M(69)	5.34 (16.2)	3.24	3.76	58.5 (15.1)	41.46 (122.9)	23.38
4a	Me	m(31)	5.26 (18.6)	3.74	3.81	58.6 (15.3)	41.99 (131.7)	24.34
4b	Et	M(73)	5.29 (16.7)	4.20	4.29	58.6 (15.4)	41.23 (122.7)	23.42
4b	Et	m(27)	5.21 (19.3)	3.78	3.88	58.34 (14.9)	41.74 (133.6)	24.73
4c	^t Bu	Ň	5.08 (18.1)	1.04	1.60	59.15 (15.7)	40.6 (123.1)	23.17

spectrum of compound 4a exhibits two single sharp lines (δ 3.74 and 3.81) arising from the metoxy group in the *E*-rotamer and two single sharp resonances at 3.24 and 3.76 ppm for methoxy groups in the Zrotamer. The shift at 3.24 of methoxy group of the Z-rotamer is shielded, due to the anisotropic effect of the phenyl group of triphenylphosphine. This effect confirms that the (E)-4 and (Z)-4 rotamers could appear as the minor and major forms, respectively, with respect to the experimental abundance percentage of both isomers that have been reported in the experimental section. Also signals for methine protons at δ = 5.34 and 5.26 ppm, which appear as two doublets for the N–CH group, respectively, for the major and minor geometrical isomers. The ¹³C NMR spectrum of 4a exhibited 44 distinct resonances that are in a good agreement with the mixture of two rotational isomers. Although the presence of the ³¹P nucleus complicates both the ¹H and ¹³C NMR spectra of 4a, it helps in assignment of the signals by long-range couplings with the ¹H and ¹³C nuclei (see the experimental section). The ¹H and ¹³C NMR spectra of (4b-c) are similar to those of 4a, except for the ester groups, which exhibited characteristic resonances with appropriate chemical shifts (see the experimental section). The ¹H and ¹³C NMR spectral data for compounds (4a-b) are consistent with the geometrical isomers. The structural assignments made on the basis of the 1H and 13C NMR spectra of compounds (4a-c) were supported by the IR spectra. The carbonyl region of the spectra exhibited two distinct absorption bands for each compound (see the experimental section). Of special interest is the ester

FIGURE 3 Proposed mechanism for the reaction between 1, 2 (2a, 2b, or 2c), and 3 for generation of phosphorus ylides 4 (4a–4c).

absorption at 1735-1624 cm⁻¹ for these compounds. Conjugation with the negative charge appears to be a plausible factor in the reduction of the wave numbers of the carbonyl absorption bands.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles [2–6], it is reasonable to assume that phosphorus ylide **4** results from the initial addition of triphenylphosphine **1** to the acetylenic ester **2** (rate constant k_2) and subsequent protonation of the 1:1 adduct (I₁) by the NH-acid **3** (rate constant k_3) to form phosphoranes **4** (rate constant k_4) (see Fig. 3).

EXPERIMENTAL

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Melting points, IR, and UV spectra of all compounds were measured on an Electrothermal 9100 apparatus, a Shimadzu IR-460 spectrometer, and a Cary UV-vis spectrophotometer model Bio-300 with a 10-mm light-path quartz spectrophotometer cell, respectively. In addition, the ¹H, ¹³C, and ³¹P NMR spectra were obtained from a Bruker DRX-300 Avance instrument with CDCl₃ as a solvent at 300.1, 121.4, and 75.5 MHz, respectively. The mass spectra were recorded on a Shimadzu QP 1100 EX mass spectrometer, operating at an ionization potential of 70 eV. Elemental analyses for C, H, and N were performed using a Heraeus CHM-O-Rapid analyzer. Dialkyl acetylenedicarboxylates, triphenylphosphine, and 3,6-dibromocarbazole were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

Preparation of Dimethyl 2-(3,6-dibromocarbazole -1-yl)-3-(triphenylphosphoranylidene)-butanedioate (**4a**)

General Procedure. To a magnetically stirred solution of triphenylphosphine (0.26 g or 1 mmol) and 3,6 dibromocarbazole (0.33 g or 1 mmol) in 10 mL of acetone, a solution of dimethyl acetylenedicarboxylate (0.14 g or 1 mmol) in 4 mL of acetone at -5° C for more than 10 min was dropwise added. After approximately 8 h stirring at room temperature, the product was filtered and recrystallized from acetone. Colorless crystals. mp 205–207°C, yield 0.67 g, 94%. IR (KBr) (ν_{max} , cm⁻¹): 1735 and 1626 (C=O). MS (m/z, %): 729 (M, 20), 467 (M-PPh₃, 34), 407 (M-C₁₂H₆NBr₂, 7), 262 (PPh₃, 60), 183 (PPh₂, 79), 108 (PPh, 52). Anal. calcd for C₃₆H₂₈Br₂NO₄P (729): C, 59.16; H, 3.86; N, 1.92%. Found: C, 59.26; H, 3.84; N, 1.92%.

Major isomer (*Z*)-**4a** (69%), ¹H NMR (300.1 MHz, CDCl₃) δ : 3.24 and 3.76 (6H, 2s, 2OCH₃), 5.34 (1H, d, ³*J*_{PH} = 16.2 Hz, P=C–CH), 7.25–7.49

(19 H_{arom} , $3C_6H_5$, and $C_{12}H_4N$), 8.01(1 H_{bro} , H_a), 8.08 (1 H_{bro} , H_b): ¹³C NMR (75.5 MHz, CDCl₃) δ : 41.46 (d, ¹ $J_{PC} = 122.9$ Hz, P=C), 49.53 and 52.87 (2OCH₃), 58.50 (d, ² $J_{PC} = 15.1$ Hz, P=C–CH), 111.90, 112.02, 112.30, 122.35, and 123.81 (10C, $C_{12}H_8N$), 125.88 (d, ¹ $J_{PC} = 91.7$ Hz, C_{ipso}), 128.81 (d, ³ $J_{PC} = 12.3$ Hz, C_{meta}), 132.19 (C_{para}), 133.31 (d, ² $J_{PC} = 9.7$ Hz, C_{ortho}), 138.96 (1C, $C_{12}H_6N$), 169.39 (d, ³ $J_{PC} = 12.2$ Hz, C=O), 171.93 (d, ² $J_{PC} = 15.7$ Hz, P–C=C). ³¹P NMR (121.5 MHz, CDCl₃) δ : 23.38 (Ph₃P⁺–C).

Minor isomer (*E*)-**4a** (31%), ¹H NMR (500.1 MHz, CDCl₃) δ : 3.74 and 3.81 (6H, 2s, 2OCH₃), 5.26 (1H, d, ³*J*_{PH} = 18.6 Hz, P=C–CH), 7.25–7.49 (19 H_{arom}, 3C₆H₅, and C₁₂H₄N), 8.04(1H_{bro}, H_a), 8.09 (1H_{bro}, H_b). ¹³C NMR (75.5 MHz, CDCl₃) δ : 41.99 (d, ¹*J*_{PC} = 131.7 Hz, P=C), 50.67 and 52.60 (2OCH₃), 58.64 (d, ²*J*_{PC} = 15.3 Hz, P=C–CH), 111.95 and 112.07, 112.33, 122.47, and 123.96 (10C, C₁₂H₈N), 125.27 (d, ¹*J*_{PC} = 91.9 Hz, C_{ipso}), 128.76 (d, ³*J*_{PC} = 11.8 Hz, C_{meta}), 132.15 (C_{para}), 133.44 (d, ²*J*_{PC} = 9.7 Hz, C_{ortho}), 139.28 (1C, C₁₂H₈N), 169.97 (d, ³*J*_{PC} = 17.1 Hz, C=O), 170.83 (d, ²*J*_{PC} = 14.9 Hz, P–C=C). ³¹P NMR (121.5 MHz, CDCl₃) δ : 24.34 (Ph₃P⁺–C).

Diethyl 2-(3,6- dibromocarbazole -1-yl)-3-(*triphenylphosphoranylidene*)-*butanedioate* (**4b**)

Colorless crystals. mp 177–179°C, yield 0.69 g, 92%. IR (KBr) (ν_{max} , cm⁻¹): 1730 and 1624 (C=O). MS (*mlz*, %): 586 (M-2OEt and Br, 33), 557 (M-2OEt and PPh, 76), 493 (M-PPh₃, 9), 325 (M-C₁₂H₆NBr₂ and PPh, 59), 262 (PPh₃, 60), 183 (PPh₂, 76), 108 (PPh, 40). Anal. calcd for C₃₈H₃₂Br₂NO₄P (757): C, 60.14; H, 4.25; N, 1.85. Found: C, 60.24; H, 4.23; N, 1.85.

Major isomer (Z)-4b (73%), ¹H NMR (300.1 MHz, CDCl₃) δ : 0.50 and 1.23 (6H, 2t, ${}^{3}J_{\text{HH}} = 7.1$ Hz, CH₃ in 2OCH₂CH₃), 4.20 and 4.29 (4H, 2 m, 2ABX₃system, and CH₂ in 2OCH₂CH₃), 5.29 (1H, d, ${}^{3}J_{PH} = 16.7$ Hz, P=C-CH), 7.23-7.53 (19H_{arom}, 3C₆H₅, and C₁₂H₄NBr), 8.02 (1H, H_a), 8.06 (1H, H_b). ¹³C NMR (75.5 MHz, CDCl₃) δ : 14.08 and 14.22 $(20CH_2CH_3)$, 41.23 (d, ${}^{1}J_{PC} = 122.7$ Hz, P=C), 58.14 (OCH_2CH_3) , 58.57 (d, ${}^2J_{PC} = 15.4$, Hz, P=C-CH), 61.60 (OCH₂CH₃), 111.81, 122.27, and 122.42 (6C, $C_{12}H_8N$), 126.11 (d, ${}^{1}J_{PC} = 91.6$ Hz, C_{ipso}), 128.33 (2C, $C_{12}H_6N$), 128.71 (d, ${}^{3}J_{PC} = 12.3$ Hz, C_{meta}), 132.04 $(2C, C_{12}H_6N), 132.11 (C_{para}), 133.38 (d, {}^2J_{PC} = 9.7 Hz,$ C_{ortho}), 139.11 (2C, $C_{12}H_6N$), 168.97 (d, ${}^{3}J_{PC} = 12.2$ Hz, C=O), 171.25 (d, ${}^{2}J_{PC} = 15.5$ Hz, P–C=C). ${}^{31}P$ NMR (121.5 MHz, CDCl₃) δ: 23.42 (Ph₃P⁺-C).

Minor isomer (*E*)-**4b** (27%), ¹H NMR (300.1 MHz, CDCl₃) δ: 1.25 and 1.35 (6H, 2t, ${}^{3}J_{HH} = 7.00$ Hz, CH₃ in 2OCH₂CH₃), 3.78 and 3.88 (4H, 2 m, 2ABX₃system, CH₂ in 2OCH₂CH₃), 5.21 (1H, d, ${}^{3}J_{PH} = 19.3$ Hz, P=C–CH), 7.23–7.53 (19H_{arom},

3C₆H₅, and C₁₂H₄NBr), 8.05 (1H, H_a), 8.06 (1H, H_b). ¹³C NMR (75.5 MHz, CDCl₃) δ : 14.99 and 15.33 (2OCH₂CH₃), 41.74 (d, ¹J_{PC} = 133.6 Hz, P=C), 58.34 (d, ²J_{PC} = 14.9 Hz, P=C–CH), 58.94 and 61.38 (2OCH₂CH₃), 111.97, 122.42, and 123.96 (6C, C₁₂H₈N), 125.58 (d, ¹J_{PC} = 92.0 Hz, C_{ipso}), 128.45 (2C, C₁₂H₆N), 128.78 (d, ³J_{PC} = 12.2 Hz, C_{meta}), 132.00 (2C, C₁₂H₆N), 132.08 (C_{para}), 133.44 (d, ²J_{PC} = 9.7 Hz, C_{ortho}), 139.42 (2C, C₁₂H₆N), 169.83 (d, ³J_{PC} = 13.5 Hz, C=O), 171.09 (d, ²J_{PC} = 14.2 Hz, P–C=C). ³¹P NMR (121.5 MHz, CDCl₃) δ : 24.73 (Ph₃P⁺–C).

Di-tert-buthyl 2-(3,6- *dibromocarbazole -1-yl)-3triphenylphosphoranylidene)-butanedioate* (**4c**)

Colorless crystals. mp 135–137°C, yield 0.77 g, 95%. IR (KBr) (ν_{max} , cm⁻¹): 1735 and 1628 (C=O). MS (*m*/*z*, %): 549 (M-PPh₃, 31), 347 (M-PPh₃ and CO₂Me₃, 7), 262 (PPh₃, 77), 183 (PPh₂, 77), 108 (PPh, 58). Anal. calcd for C₄₂H₄₀Br₂NO₄P (813): C, 62.12; H, 4.88; N, 1.68. Found: C, 61.99; H, 4.92; N, 1.72.

Major isomer (*Z*)-**4c** ¹H NMR (300.1 MHz, CDCl₃) δ : 1.04 and 1.60 (18H, 2s, 2CMe₃), 5.08 (1H, d, ³*J*_{PH} = 18.1 Hz, P=C–CH), 7.23–7.56 (19H_{arom}, 3C₆H₅, and C₁₂H₄NBr), 8.01 (¹H, H_a), 8.04 (¹H, H_b): ¹³C NMR (75.5 MHz, CDCl₃) δ : 28.22 and 28.44 (2CMe₃), 40.60 (d, ¹*J*_{PC} = 123.1 Hz, P=C), 59.15 (d, ²*J*_{PC} = 15.7 Hz, P=C–CH), 77.67 and 81.09 (2OCMe₃), 111.78, 118.01, 122.17, and 123.82 (8C, C₁₂H₈N), 126.57 (d, ¹*J*_{PC} = 91.2 Hz, C_{ipso}), 128.32 (1C, C₁₂H₆N), 128.52 (d, ³*J*_{PC} = 12.2 Hz, C_{meta}), 131.97 (d, ⁴*J*_{PC} = 2.1 Hz, C_{para}), 133.44 (d, ²*J*_{PC} = 9.7 Hz, C_{ortho}), 139.61 (2C, C₁₂H₆N), 168.60 (d, ³*J*_{PC} = 11.8 Hz, C=O), 169.61 (d, ²*J*_{PC} = 14.7 Hz, P–C=C). ³¹P NMR (121.5.4 MHz, CDCl₃) δ : 23.17 (Ph₃P⁺–C).

KINETIC STUDIES

The synthetic reactions between triphenylphosphine 1, dialkyl acetylenedicarboxylates 2, and CH, SH, or NH-acids have been reported earlier [17–34], but the kinetic study of these reactions has not been yet investigated. Herein, we describe a kinetic investigation of the current synthesis. Numerous kinetic investigations over a large area of different reactions have been reported previously using UV analysis [35–40]. To gain further insight into the reaction mechanism, a kinetic study of the reactions was undertaken by UV spectrophotometric technique. 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 solution of compounds 1, 2c, and 3 was prepared in 1,4dioxane as a solvent. Approximately, 3 mL aliquot from each reactant was pipetted into a 10-mm light



FIGURE 4 The UV spectra of the reaction between **1**, **2c**, and **3** with 10^{-3} M concentration of each compound as reaction proceeds in 1, 4-dioxane with 10 mm light-path cell.

path quartz spectrophotometer cell, and the relevant spectra were recorded over the wavelength range 190-400 nm. In a second experiment, a 1-mL aliquot from the 3 $\times 10^{-3}$ M solutions of each compound of 1 and 3 was pipetted first into a quartz spectrophotometer cell (as there is no reaction between them), later 1-mL aliquot of the 3 $\times 10^{-3}$ M solution of reactant 2c was added to the mixture and the reaction monitored by recording scans of the entire spectra every 13 min over the whole reaction time at ambient temperature. The ultraviolet spectra shown in Fig. 4 are typical. From this, the appropriate wavelength was found to be 368 nm (corresponding mainly to product 4c). Because at this wavelength, compounds 1, 2c, and 3 have relatively no absorbance value. This, then provided the opportunity to fully investigate the kinetics of the reaction between triphenvlphosphine 1, di-tert-butyl acetylenedicarboxylate 2c, and 3, 6-dibromocarbazole 3 at 368 nm in the presence of 1,4-dioxane as solvent. Because 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 \times 10^{-4} M \leq M_{4c} \leq 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.

For each kinetic experiment, first a 1-mL aliquot from each freshly made 3×10^{-3} M solution of compounds **1** and **3** in 1,4-dioxane was pipetted into a quartz cell, and then a 1-mL aliquot of the 3×10^{-3} M of solution of reactant **2c** was added to the mixture, keeping the temperature at 12.0°C. The reaction kinetics was followed by plotting UV absorbance against time. Figure 5 shows the absorbance change (dotted line) versus time for the 1:1:1 addition re-



FIGURE 5 Second-order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between compounds **1**, **2c**, and **3** at 368 nm and 12.0° C in 1,4-dioxane.

action between compounds 1, 2c, and 3 at 12.0°C. The infinity absorbance (A_{∞}) that is the absorbance at reaction completion can be obtained from Fig. 5 at t = 214 min. With respect to this value, zero, first, or second curve fitting could be drawn automatically for the reaction by the software [41] 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 Fig. 5. Thus, the reaction between triphenylphosphine 1, di*tert*-butyl acetylenedicarboxylate **2c**, and **3** follows second-order kinetics. The second-order rate constant (k_2) is then automatically calculated using a standard equation [41] within the program at 12.0°C. It is reported in Table 2.

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

TABLE 2Values of Overall Second-Order Rate Constant forthe Reaction Between 1, 2c, and 3 in the Presence of SolventsSuch As 1,4-Dioxane, Ethyl Acetate, and 1,2-Dichloroethane,Respectively, at All Temperatures Investigated

		$k_2 (M^{-1} min^{-1})$			
Solvent	δ	12.0°C	17.0°C	22.0°C	27.0°C
1,4-Dioxane Ethyl acetate 1,2-Dichloroethane	2 6 10	56.8 67.0 78.8	70.1 81.3 93.1	82.3 93.6 109.3	98.8 109.7 123.6

previous experiment. In addition, the overall order of reaction was also two.

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, ethyl acetate and 1,2-dichloroethane with 6- and 10-dielectric constants, respectively, were chosen as suitable solvents because they could not only 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 2. The results show that the rate of reaction in each case was increased at higher temperature. In addition, the rate of reaction between 1, 2c, and 3 was accelerated in a higher dielectric constant environment (1,2-dichloroethane) in comparison with a lower dielectric constant environment (1,4-dioxane) 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, giving activation energies of reaction between 1, 2c, and 3 (25.8 kJ/mol) from the slope of Fig. 6.

Effect of the Concentration

To determine the reaction order with respect to triphenylphosphine 1 and dialkyl acetylenedicarboxylate 2(2c), in the continuation of experiments, all kinetic studies were carried out in the presence



FIGURE 6 Dependence of second-order rate constant (ln k_2) on reciprocal temperature for the reaction between **1**, **2c**, and **3** measured at wavelength 368 nm in 1,4-dioxane in accordance with the Arrhenius equation.



FIGURE 7 Pseudo-first-order fit curve (full line) for the reaction between **2c** and **3** in the presence of excess **1** (10^{-2} M) at 368 nm and 12.0°C in 1,4-dioxane.

of excess **3**. Under this condition, the rate equation may therefore be expressed as

Rate =
$$k_{obs} [1]^a [2]^\beta - k_{obs} = k_2 [3]^\gamma$$
 or
 $\ln k_{obs} = \ln k_2 + \gamma \ln [3]$ (1)

In this case $(3 \times 10^{-2} \text{ M of } 3 \text{ instead of } 3 \times 10^{-3} \text{ M})$, using the original experimental absorbance versus time data provides a second-order fit curve (full line) against the time at 368 nm that exactly fits the experimental curve. The value of the rate constant was the same as that of obtained from the previous experiment (3 $\times 10^{-3}$ M). Repetition of the experiments with 5×10^{-2} M and 7×10^{-2} M concentrations of **3** gave, separately, the same fit curve and the rate constant. In fact, the experimental data indicated that the observed pseudo-second-order rate constant (k_{obs}) is equal to the second-order rate constant (k_2) , this is possible when γ is zero in Eq. (1). It is appeared, therefore, that the reaction is zero and second order with respect to 3 (NH-acid) and the sum of 1 and 2 (2c) ($\alpha + \beta = 2$), respectively. To determine the reaction order with respect to dialkyl acetylenedicarboxilate 2 (2c), the continuation of experiment was performed in the presence of excess 1

$$Rate = \mathcal{K}_{obs}[3]^{\gamma}[2]^{\beta}$$
$$\mathcal{K}_{obs} = k_{2}[1]^{\alpha}$$
(2)

The original experimental absorbance versus time data provides a pseudo-first-order fit curve at 368 nm, which exactly fits the experimental curve (dotted line) as shown in Fig. 7. As a result, since $\gamma = 0$ (as determined previously), it is reasonable to accept that the reaction is first order with respect to the compound **2** (**2c**) ($\beta = 1$).

Because the overall order of reaction is $2 (\alpha + \beta + \gamma = 2)$, it is obvious that $\alpha = 1$ and the order of triphenylphosphine **1** must be equal to 1. This observation was also obtained for reactions between (**1**, **2b**, and **3**) and (**1**, **2a**, and **3**). Based on the above results, a simplified proposed reaction mechanism is shown in Fig. 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:

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

The steady-state assumption can be employed for $[I_1]$ that generates the following equation:

$$[\mathbf{I}_1] = \frac{k_2[1][2]}{k_{-2} + k_3[3]}$$

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

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

Because 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 low becomes

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

The last equation indicates that the overall reaction order is three, which is not compatible with the experimental overall reaction order (two). In addition, according to this equation, the order of reaction with respect to 3,6-dibromocarbazole 3 is one, whereas it was actually shown to be equal to zero. For this reason, it appears 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 carbazole ion (N^-) . The phosphonium and carbazole ions, as we see in Fig. 3, have full positive and negative charges and form very powerful ion-dipole bonds to 1,2-dichloroethane, the high dielectric constant solvent. However, the transition state for the reaction between the two ions carries a dispersed charge, which here is divided between the attacking carbazole and the phosphonium ions. A bonding of solvent (1,2-dichloroethane) to this dispersed charge would be much weaker than to the concentrated charge of carbazole and phosphonium ions. The solvent thus would stabilize the species ions more than it does 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 the steady-state assumption can be expressed by

Rate =
$$k_4[I_2][N^-]$$
.

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

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

This equation is independent of the rate constant of 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) is very fast [42–45]. 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 (Fig. 3), have no charge and could not form strong ion-dipole bonds to the high dielectric constant solvent, 1,2dichloroethane. 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 to the reactants, which lack the charge. The solvent thus stabilizes the transition state more than it does the reactants and, therefore, $E_{\rm a}$ is reduced that speeds up the reaction. Our experimental results show that the solvent with the higher dielectric constant exerts a powerful 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 with lower dielectric constant (1,4-dioxane, see Tables 2-4). The results of the present work (effects of the solvent and the 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 (2a, 2b, or 2c), and 3,6-dibromocarbazole 3. Two steps involving 3 and 4 are not the rate-determining step although the discussed effects, taken altogether, are compatible with the 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

TABLE 3 Values of Overall Second-Order Rate Constant for the Reaction Between 1, 2b, and 3 in the Presence of Solvents Such As 1,4-Dioxane, Ethyl Acetate, and 1,2-Dichloroethane, Respectively, at All Temperatures Investigated

Solvent		$k_2(M^{-1} min^{-1})$				
	δ	12.0°C	17.0°C	22.0°C	27.0°C	
1,4-Dioxane Ethyl acetate 1,2-Dichloroethane	2 6 10	319.2 350.2 437.5	355.1 387.1 452.6	381.5 423.0 507.3	413.3 452.3 557.4	

experimental result using a mechanistic scheme based on 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. 3) is given by

$$\frac{\mathrm{d}[4]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{ylide}]}{\mathrm{d}t} = \mathrm{Rate} = k_4[\mathrm{I}_2][\mathrm{N}^-] \qquad (5)$$

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

$$\frac{d[\mathbf{I}_1]}{dt} = k_2[1][2] - k_{-2}[\mathbf{I}_1] - k_3[\mathbf{I}_1][3]$$
$$\frac{d[\mathbf{I}_2]}{dt} = k_3[\mathbf{I}_1][3] - k_4[\mathbf{I}_2][\mathbf{N}^-]$$

To obtain a suitable expression for $[I_2]$ to put into Eq. (5), we can assume that, after an initial brief period, the concentrations of $[I_1]$ and $[I_2]$ become a steady state with their the rates of formation and the rates of disappearance are just balanced. Therefore, d[I₁]/dt and d[I₂]/dt are zero and we can obtain expressions for $[I_2]$ and $[I_1]$ as follows:

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

$$\frac{d[I_1]}{dt} = 0$$

$$[I_1] = \frac{k_2[1][2]}{k_{-2} + k_3[3]}$$
(7)

TABLE 4Values of Overall Second-Order Rate Constant for
the Reaction Between 1, 2a, and 3 in the Presence of Solvents
Such As 1, 4-Dioxan, Ethyl Acetate, and 1, 2-Dichloroethane,
Respectively, at All Temperatures Investigated

Solvent		$k_2 (M^{-1} min^{-1})$				
	δ	12.0°C	17.0°C	22.0°C	27.0°C	
1,4-Dioxane Ethyl acetate 1,2-Dichloroethane	2 6 10	432.1 478.6 548.3	475.3 517.8 573.5	505.1 540.2 617.7	541.8 596.7 669.2	

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

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

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

Rate =
$$\frac{k_2 k_3 k_4 [1] [2] [3] [N^-]}{k_4 [N^-] [k_{-2} + k_3 [3]]}$$
 or
Rate = $\frac{k_2 k_3 [1] [2] [3]}{[k_{-2} + k_3 [3]]}$ (8)

Since the experimental data have 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 =
$$k_2[1][2]$$
 (9)

This equation, which was obtained from a mechanistic scheme (shown in Fig. 3) by applying the steadystate approximation, is compatible with the results obtained by UV spectrophotometry.

Further Kinetic Investigations

Effect of Structure of Dialkyl Acetylenedicarboxylates. To confirm the above observations, further experiments were performed with diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a**, 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**, **2b**, and **3**) and (**1**, **2a**, and **3**) are reported in Tables 3 and 4, respectively, for all solvents and temperatures investigated. The original experimental absorbance curves (dotted line) accompanied by the second-order fit curves (full line), which exactly fit experimental curves (dotted line), for both reactions are shown in Figs. 8 and 9 at 12.0°C and 368 nm.

As can be seen from Tables 3 and 4, the behavior of diethyl acetylenedicarboxylate **2b** and dimethyl acetylenedicarboxylate **2a** is the same as for di-*tert*butyl acetylenedicarboxylate **2c** (Table 2) with respect to the reaction with triphenylphosphine **1** and 3,6-dibromocarbazole **3**. 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 five to seven times more than for the reaction with di-*tert*-butyl acetylenedicarboxylate **2c**



FIGURE 8 Second-order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between **1**, **2b**, and **3** at 368 nm and 12.0°C in 1, 4-dioxane.



FIGURE 9 Second-order fit curve (full line) accompanied by the original experimental curve (dotted line) for the reaction between 1, 2a, and 3 at 368 nm and 12.0°C in 1, 4-dioxane.

(see Tables 2–4). It seems that both inductive and steric factors for the bulky alkyl groups in **2c** tend to reduce the overall reaction rate (see Eq. (9)). In the case of dimetyl acetylenedicarboxylate **2a**, the lower steric and inductive effects of the dimethyl groups exert a powerful effect on the rate of reaction.

CONCLUSIONS

Briefly, we prepared novel phosphorus ylides using a one-pot reaction between triphenylphosphine **1** and dialkyl acetylenedicarboxylates **2** (**2a**, **2b**, or **2c**) in the presence of a NH-acid such as 3,6dibromocarbazole **3**. The present method has the advantage that not only the reaction is performed under neutral conditions but also the substances can be mixed without any activation or modifications. The stable phosphorus ylides 4 (4a, 4b, or 4c) are potentially useful synthetic intermediates, and the procedure described here may be acceptable for the preparation of phosphoranes with variable functionalities. In addition, kinetic investigation of these reactions was undertaken using UV spectrophotometry. The results can be summarized as follows: (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 3,6-dibromocarbazole 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 of the reaction with di-tert-butyl acetylenedicarboxylate 2c (25.8 kJ/mol) was higher than that for both the reactions, which were followed by the diethyl acetylenedicarboxylate **2b** (12.04 kJ/mol) and dimethyl acetylenedicarboxylate 2a (10.47 kJ/mol) in 1,4-dioxane. (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 the rate-determining step (k_2) , and this was confirmed based on the steady-state approximation.

SUPPLEMENTARY MATERIAL

Proposed mechanism for the reaction between 1, 2 (2a, 2b, or 2c), and 3 for generation of phosohorus ylides 4 (4a, 4b, or 4c), figures showing the UV spectrum of 10^{-3} M of 1, 2c, and 3, and the experimental absorbance change versus time for the reaction between 2c and 3 in the presence of excess 1 (10^{-2} M) at 368 nm and 12.0° C in 1,4-dioxane are available from the corresponding author (smhabibi@chem.usb.ac.ir) on request.

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