Kinetics and mechanism of gas-phase pyrolysis of ylides. Part 2.[1] Analysis and comparison of reactivity of benzoyl-stabilized triphenylphosphonium and triphenylarsonium methylides

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Abstract

Six triphenylphosphonium benzoylmethylides and four arsonium analogues were synthesized and characterized. The kinetics of gas-phase pyrolysis of these compounds was investigated over the temperature range 386–545 K for the phosponium ylides and 419–556 K for the arsonium ylides. The products of both sealed-tube pyrolysis and flash vacuum pyrolysis were analyzed and compared. The values of the Arrhenius log A and E_a are, respectively, 12.6 ± 1.4 s^{-1} and 134.5 ± 5.3 $kJmol^{-1}$ for the phosphorane, and 10.4 ± 0.7 s^{-1} and 124.5 ± 17.8 $kJmol^{-1}$ for the arsorane compounds. A mechanism involving the extrusion of Ph_3PO in case of the phosponium ylides, and the extrusion of Ph_3AsO or Ph_3As in case of arsonium ylides is proposed and used to rationalize the molecular reactivities of the ylides under study, and to draw comparisons between the rate constants of pyrolysis at 500 K of the analogous phosphonium and arsonium ylides.

Keywords: Pyrolysis, gas-phase, ylides, kinetics, mechanism

Introduction

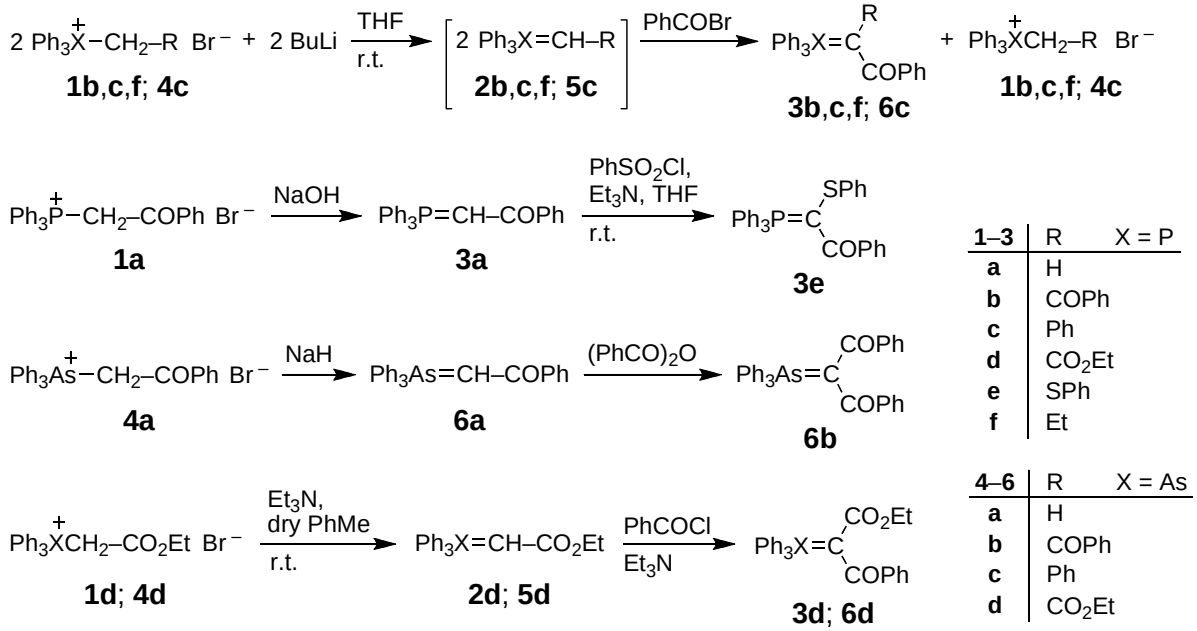
Flash vacuum pyrolysis (FVP) of phosphonium α-acylmethylides has been successfully used to prepare alkynes and provide an important route to this functional group.[2] FVP also found many other applications in organic synthesis, incluing the preparation of novel heterocycles.[3–5] Earlier studies on FVP frequently included formulation of reaction mechanisms. However, only recently we have provided the first kinetic analysis of gas-phase pyrolysis of stabilized phosphonium ylides to correlate reactivity with structure, to elucidate structural effects and to lend support to proposed mechanisms.[1,6] Besides, there seem to be no reports in the literature on either kinetic or mechanistic studies on the gas-phase pyrolysis of carbonyl-stabilized arsonium ylides, and the only research in this field appears to be on the pyrolysis of triphenylarsonium α-benzoyl-methylide in boiling toluene and its reaction with unsaturated ketones and esters.[7,8] Lack of interest in gas-phase pyrolysis of arsonium ylides is to be expected because of the hazards

associated with arsenic compounds. The structure, synthesis and thermal gas-phase reactions of stabilized phosphorus ylides continue to be investigated.[1,6] Parallel studies on arsonium ylides are pending. Furthermore, structural, kinetic and mechanistic studies on arsonium ylides are expected to help to elucidate and compare the chemistry of phosponium and sulfonium ylides.[8,9]

Results and Discussion

Syntheses

Phosphonium ylides **3b**,**c**,**f** and arsonium ylide **6c** were prepared by the reaction of the respective quaternary bromide salts **1b**,**c**,**f** and **4c**, in dry tetrahydrofuran with butyllithium in dry hexane at room temperature under a nitrogen atmosphere followed by benzoyl bromide in dry tetrahydrofuran. The molar ratio of the reactants, quaternary bromide salts/BuLi/PhCOBr was kept at 2:2:1. Ylides **3d** and **6d** were prepared from **1d** and **4d**, respectively, using triethylamine as base instead of butyllithium; the reactant ratio was adjusted to 1:2:1. The difference in molar ratios has been rationalized in terms of the effect substituents have on the relative basicity of the intermediate ylides **2** and **5**, and the need for an external proton scavenger (BuLi) in the transylidation step leading to the target ylide when the basicity of the intermediate ylide is relatively low to affect this step.[1] Likewise, the role of the base is evident in the synthesis of ylides **3a** and **6a**: NaOH has been used for the preparation of phosphonium ylide **3a** and NaH for the synthesis of arsonium ylide **6a**.[7,10] Ylide **6b** was obtained by treating ylide **6a** with benzoic anhydride,[7] while ylide **3e** was synthesized by treating ylide **3a** with benzenesulphonyl chloride in the presence of triethylamine as base. The structure of ylide **3e** was established by X-ray analysis. The synthetic pathways for substrates **3b–d**,**e**,**f**, **and 6c**,**d** are shown in Scheme 1.



1–3	R (X = P)
a	H
b	COPh
c	Ph
d	CO_2Et
e	SPh
f	Et

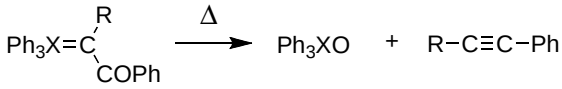
4–6	R (X = As)
a	H
b	COPh
c	Ph
d	CO_2Et

Scheme 1

Reaction products and mechanisms

Products for complete gas-phase pyrolysis were obtained for all ten substrates using: (i) FVP (flow) reactor at 500 ^{o}C; and (ii) Pyrex sealed-tube (static) pyrolyser [conventional pyrolysis (CP) method] at temperatures equal to or exceeding those used in the kinetic experiments. Besides, sealed-tube reactions were allowed sufficient residence time to ensure complete pyrolysis. The pyrolysates obtained by this method were separated using preparative liquid chromatography (PLC) and analyzed by GC-MS, FT-IR and NMR techniques. The pyrolysates from FVP were collected in traps cooled by liquid nitrogen and were analyzed similarly. It is noteworthy that both the FVP and CP reactions gave identical products. The thermal elimination fragments from each substrate were simply an organo-phosphorus or arsenic fraction alongside an alkyne or ketone compound; the yields were quantitative.

Upon pyrolysis all triphenylphosonium α-benzoylmethylides **3a**–**f** gave only triphenylphosphine oxide (the phosphorus-containing fragment, X = P) and an R-substituted phenylalkyne as shown in Scheme 2.

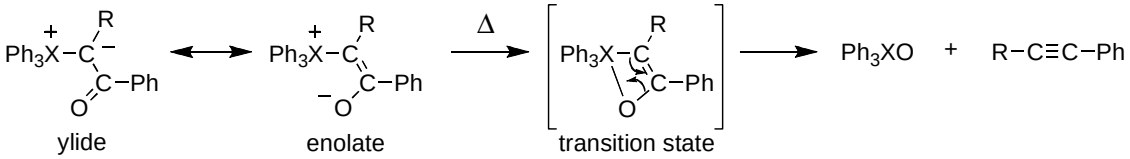


3a–f, X = P
6b–d, X = As

R = **a**: H, **b**: COPh, **c**: Ph, **d**: CO_2Et, **e**: SPh, **f**: Et

Scheme 2

The structural rationale for the extrusion of triphenylphosphine oxide from stabilized ylides, which is based on the experimental coupling constants observed for P and α-carbonyl carbon suggests resonance contributors one of which is an enolate form.[6] The extrusion of triphenylphosphine oxide from the enolate structure proceeds through the formation of a four-membered transition state (X = P) as shown in Scheme 3.



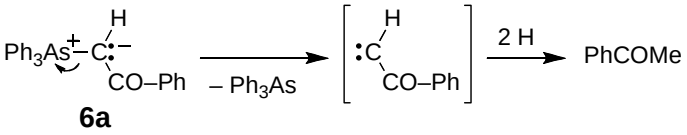
3a–f, X = P
6b–d, X = As

R = **a**: H, **b**: COPh, **c**: Ph, **d**: CO_2Et, **e**: SPh, **f**: Et

Scheme 3

The behavior of the triphenylarsonium α-benzoylmethylides during pyrolysis is affected by the relative stability and the carbanion nature of the ylide, the lower electronegativity of arsenic and its lower propensity to act as an oxygen scavenger.[7–10] The three effectively stabilized, R-

substituted triphenylarsonium α-benzoylmethylides **6b–d**, analogues of the stabilized phosphonium ylides **3b–d**, upon pyrolysis extruded triphenylarsine oxide (Scheme 2, X = As) according to the reaction pathway involving the four-membered transition state (Scheme 3, X = As). On the other hand, ylide **6a** (Ph_3As=CHCOPh), which lacks an additional stabilizing substituent, pyrolyzed to give triphenylarsine and acetophenone. To account for the pyrolysis products of this ylide a different mechanism is suggested: Extrusion of triphenylarsine leads to the formation of a reactive carbene intermediate (Scheme 4); capture of hydrogen by the carbene intermediate results in the formation of acetophenone.[1]



6a

Scheme 4

To provide support for the proposed mechanism, pyrolysis of ylide **6a** was conducted in the presence of cyclohexene as radical trap. Under these conditions no acetophenone was obtained, and triphenylarsine was the only product which could be adequately identified. Kinetic data provided further evidence for the possible involvement of a reactive carbene pathway. The arsonium ylide **6a** was found to be the most reactive in the arsonium series **6a**–**d**, whereas the analogous phosphonium ylide **3a** was the least reactive in the series **3a**–**f**. Furthermore, the pyrolysates of ylide **6c** contained minor fractions of triphenylarsine and deoxybenzoin together with the major fractions of triphenylarsine oxide and diphenylacetylene. These results suggest the involvement of both the four-membered transition state (major pathway) and the reactive carbene pathway (minor), and hence provide an explanation for the fact that ylide **6c** was found to be slightly more reactive than its phosphorus analogue **3c**.

Kinetics and relative molecular reactivities

The kinetic data for ylides **3a**–**f** and **6a**–**d** are listed in Table 1. The reactions of these compounds followed a first-order rate equation. Each rate constant at any one temperature represents an average from a set of at least three measurements that are in agreement to within ±2% rate spread. To ensure reliable kinetic results, the pyrolysis of each substrate was followed over a temperature range of ca 48±10 K and 95±5% reaction.[5,16,17] Rates were obtained by monitoring the disappearance of substrates. The Arrhenius log A/$s^{-1}$and activation energy (Ea/kJ mol^{-1}), the entropy of activation ($\Delta S^{\#}$/J K^{-1} mol^{-1}), and the rate constant at 500 K for the reactions of the compounds under study are also recorded in Table 1.

The Arrhenius pre-exponential factor log A = 10–14 s^{-1} and activation energy E_a = 107–142 kJmol^{-1} are in the range expected for unimolecular thermal gas-phase elimination reactions.[1,5,16,17] The entropy values of activation $\Delta S^{\#}$ [JK^{-1} mol^{-1}] are negative or small positive (ylide **3b**) suggesting high structural organization and an ordered transition state of reaction.

Table 1. Rate constants k, Arrhenius log A and E_a, entropy of activation $\Delta S^{\#}$, and rate constants at 500 K of gas-phase pyrolysis of benzoyl-stabilized ylides **3a**–**f** and **6a**–**d**

3	R	T [K]	10^4 k [s^{-1}]	log A [s^{-1}]	E_a [kJmol^{-1}]	10^4 k_{500K} [s^{-1}]	$\Delta S^{\#}_{500K}$ [$JK^{-1}mol^{-1}$]
a	H	500.25	3.384	10.29 ± 0.40	131.7 ± 4.0	3.442	- 52.21
		511.05	7.406				
		521.15	11.74				
		533.35	25.19				
		544.25	45.21				
b	COPh	385.85	0.712	13.99 ± 0.29	134.1 ± 2.3	9480	+ 18.58
		401.95	3.370				
		407.75	6.255				
		413.35	10.69				
		418.15	18.53				
		422.85	25.67				
		426.75	38.12				
c	Ph	453.70	3.420	11.37 ± 0.40	129.1 ± 3.7	76.28	- 31.55
		462.60	6.100				
		471.40	10.33				
		479.35	20.22				
		488.60	38.96				
		497.75	66.54				
d	CO_2Et	463.90	1.730	11.29 ± 0.25	133.6 ± 2.3	21.38	- 33.14
		473.20	3.400				
		483.50	7.550				
		493.20	13.70				
		503.30	25.78				
e	SPh	454.55	0.732	11.16 ± 0.12	133.1 ± 1.1	17.96	- 35.56
		469.65	2.238				
		483.55	6.182				
		492.65	11.35				
		497.45	14.54				
		504.25	23.16				
		511.15	37.01				
f	Et	483.25	5.841	11.87 ± 0.26	139.8 ± 2.5	18.63	- 22.01
		490.15	9.607				
		496.25	13.72				
		500.85	20.49				
		510.95	37.79				
		517.75	59.46				

Table 1. Continued

6	R	T [K]	10^4 k [s^{-1}]	log A [s^{-1}]	E_a [kJmol^{-1}]	10^4 k_{500K} [s^{-1}]	$\Delta S^{\#}_{500K}$ [$JK^{-1}mol^{-1}$]
a	H	419.15	3.347	9.79 ± 0.34	106.7 ± 2.8	440.1	-61.87
		424.15	4.285				
		428.65	5.675				
		433.95	9.337				
		441.85	14.92				
		447.15	20.94				
		456.15	38.12				
b	COPh	493.65	2.326	10.40 ±0.49	132.6 ± 4.8	3.546	-50.12
		505.85	5.127				
		513.15	7.709				
		517.25	11.46				
		526.20	16.18				
		532.35	24.91				
c	Ph	419.90	0.565	9.68 ± 0.36	112.0 ± 3.2	96.94	- 63.89
		440.25	2.455				
		463.05	11.16				
		470.95	18.98				
		487.15	56.55				
		496.85	69.73				
d	CO_2Et	500.45	1.959	11.13 ±	142.3 ± 2.5	1.850	- 36.19
		509.65	3.678	0.25			
		518.65	5.950				
		531.55	13.44				
		545.10	31.36				
		555.35	58.44				

The Arrhenius plots were strictly linear over >95% reaction with correlation coefficients in the order of 0.998 ±0.001. Typical plots are shown in Figure 1 for phosphonium ylide **3b** and its arsonium analogue **6b**. The coefficients for these two correlations are 0.999 and 0.998, respectively. The rate constants at T = 500 K were calculated using the kinetic relation: log k = log A $-E_a$/4.574 T; log A and E_a, being the Arrhenius parameters obtained for the ylide reactions. The limits of error in Table 1 represent the correlation statistical values. The rate constants were computed at T = 500 K for two valid reasons: (i) this temperature is well within the range over which the present reactions were studied (namely, 386–554 K for the phosphorus series and 419–556 K for arsenic series); (ii) the rates at this temperature would allow facile comparisons of molecular reactivity to be made within and between the ylide series.

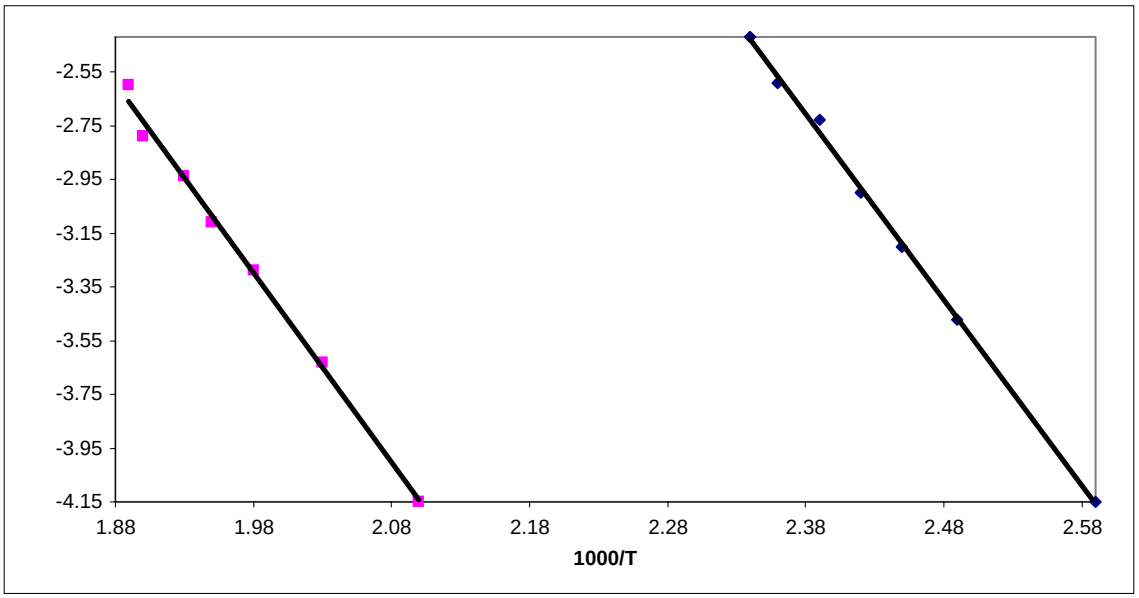


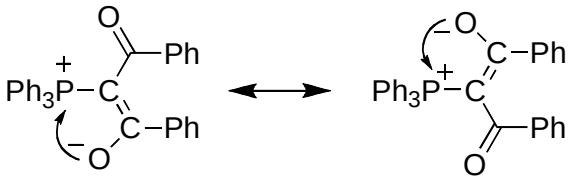
Figure 1. Arrhenius plots of log k vs. 1000/T for ylides **3b** (■ intercept = 9.79, slope = –5.57, r^2 = 0.998) and **6b** (◆ intercept = 13.99, slope = –7.01, r^2 = 0.999).

The rate constants at 500 K of pyrolysis of the benzoyl-stabilized phosphorus ylides **3a–f** are given in Table 2. The data indicate that the inductively electron-donating group (R = Et) as well as the electron-withdrawing groups (R = COPh, Ph, CO_2Et, SPh) increase rates of pyrolysis compared with hydrogen (R = H); the rate factors are, 5.41, 2.76×10^3, 22.2, 6.22, and 5.23, respectively.

Table 2. Rate constants (k/s^{-1}) at 500 K for pyrolysis of benzoyl-stabilized ylides **3a–f** and **6a–d**

3	R	10^4 k/s^{-1}	**6**	R	10^4 k/s^{-1}
a	H	3.44	**a**	H	4.40×10^2
b	COPh	9.48×10^3	**b**	COPh	3.55
c	Ph	76.3	**c**	Ph	96.9
d	CO_2Et	21.4	**d**	CO_2Et	1.85
e	SPh	18.0			
f	Et	18.6			

The relatively large rate factor of 2.76×10^3 (1.38×10^3, on statistical basis) obtained for ylide **3b** (R = COPh) is attributed to the presence of two α-carbonyl groups providing equivalent anionic oxygen moieties for potential interaction with the cationic phosphorus center leading to facile extrusion of triphenylphosphine oxide (Scheme 5) according to the mechanism suggested for the thermal elimination reaction shown in Scheme 3.



Scheme 5

As expected, the results in Table 2 also show that the stabilization of the carbanionic ylide through conjugative effects leads to higher molecular reactivities (ylides **3b**–**d**), than by an electron-withdrawing inductive effect on the carbanion (ylide **3f**) or by the influence of the electron-donating inductive effect on the enolate-like contributor of ylide **3e**. The relatively high rate factor (22.2) of ylide **3c** might be the result of the special structural feature of the phenyl group, which is able to act either as an electron-withdrawing or an electron-donating group. The relative rate factor (6.22) of ylide **3d** (R = CO_2Et) appears to be rather low compared with that (2.76×10^3) of ylide **3b** (R = COPh), even though both ylides have an additional stabilizing carbonyl group alpha to the carbanionic centre. The reason for this is partly due to the fact that the carbonyl oxygen of the ester moiety is found to lie mostly in a conformation *anti* to phosphorus, except for the simple case of **3a** (R = H).[18] An ionic oxygen *anti* to the incipient phosphorus would be expected to be less effective in the extrusion of triphenylphosphine oxide.

Table 2 also contains the results of the kinetic analysis of the thermal gas-phase elimination reaction of the arsonium ylides **6a**–**d**. Two mechanisms have been proposed for these reactions: a reaction pathway involving a four-membered transition state (Scheme 3) for ylides **6b** and **6d**, and a reactive carbene intermediate for ylide **6a**. Ylide **6c** seems to pyrolyse by both routes, but the contribution from the carbene intermediate pathway is small. The relative rates based on the data of Table 2, and the ratio of rate constants included in Table 3 are compatible with the proposed reaction mechanisms.

Table 3. Ratio of rate constants (k/s^{-1}) at 500 K of ylides **3a–d** and **6a**–**d**

R	Ylide pair	(k_P/k_{As})	(k_{As}/k_p)
H	**6a/3a**		1.28×10^2
COPh	**3b/6b**	2.67×10^3	
Ph	**6c/3c**		1.27
CO_2Et	**3d/6d**	11.6	

The trend in rates of reaction (Table 2) of the stabilized arsonium ylides **6b, 6d** is the same as for their analogous phosphonium ylides **3b, 3d**; the mechanism of pyrolysis (Scheme 3) being the same for the two sets of compounds (four-membered transition state). The reason for the higher reactivity of the phosphonium ylides (Table 3) relates to the much easier extrusion of triphenylphosphine oxide compared with triphenylarsine oxide.[7-9] The highest rate of reaction (k

= 4.4×10^2) in the arsenic series is that of ylide **6a** (R = H). The ylide has no additional stabilizing substituent, and it is this feature which accounts for the formation of the reactive carbene intermediate following the extrusion of triphenylarsine rather than triphenylarsine oxide, and also accounts for the observed high rate of reaction and higher rate ratio (Table 3). It is worth to note that arsenous is a relatively poor oxygen scavenger.[7–9,19,20] The small contribution from the carbene pathway to the overall mechanism of pyrolysis of ylide **6c** appears to be the reason why this arsonium ylide is slightly more reactive than its phosphorus analogue **3c**.

Experimental Section

General Procedures. Melting points were recorded with a Shimadzu-Gallenkamp apparatus. Mass spectra were obtained using a VG Auto-Spec-Q high resolution spectrometer coupled to a DEC 3000 Alpha AXP workstation and OPUS data system, and a Finigan Mat INCOSXL instrument for GC-MS studies (EI, 70 eV). Elemental analyses were performed on a LECO CHNS-932 analyser. IR spectra were obtained with a Fourier Transform FT-IR Perkin Elmer 2000 spectrophotometer. A Bruker DPX 400 MHz spectrometer with ^{1}H, ^{13}C and ^{31}P probes was used for NMR analyses of $CDCl_3$ solutions with TMS as reference for ^{1}H and ^{13}C, and external 85% H_3PO_4 for ^{31}P NMR. HLPC analyses were carried out on a Waters probe (pump model 515 and Schimadzu 2487 UV detector).

Sealed-tube (CP) pyrolysis was conducted in a custom-made Chemical Data System (CDS) pyrolyser comprising an aluminum block with a groove to accommodate the Pyrex sealed-tube reactor and fitted with a platinum-resistance thermometer and thermocouple connected to a Comark microprocessor thermometer. The block temperature was controlled by a Eurotherm 093 precision temperature regulator. Aluminum was chosen for its low temperature gradient and resistance to elevated temperatures. Maximum pyrolysis for product analysis was conducted at temperatures equal to or exceeding those recorded for complete pyrolysis during kinetic runs. Flash vacuum pyrolysis (FVP) was conducted in a horizontal fused-quartz tube (30×2.5 cm) housed in Büchi Kugelrohr sublimation oven. Heating was by means of a carbolite Eurotherm tube furnace MTF-12/38A, and the temperature was monitored by a Pt/Pt–13% Rh thermocouple situated at the center of the furnace. The pressure was measured by a Pirani gauge and maintained at 10^{-2} Torr using an Edwards E2M5 high capacity rotary oil pump. The estimated residence time of the sample passing through the hot zone was ca 10^{-3} s. The pyrolysates leaving the heated tube were collected in a U-shaped trap cooled in liquid nitrogen. A short residence time is deemed necessary to prevent secondary decomposition.

Precursors, materials, and precautions. The quaternary phosphonium and arsonium salts **1** and **4** required for the synthesis of ylides **3a**–**f** and **6a**–**d** were prepared following literature procedures, and were characterized based on mp, ^{1}H, ^{13}C, ^{31}P NMR and MS data.[10–15]

Triphenylphosphine (10.5 g, 0.04 mol) or triphenylarsine (12.2 g, 0.04 mol) and the appropriate alkyl bromide (0.04 mol) were refluxed in toluene (60 mL) for 4–5 h.[11,12] The quaternary arsonium salt **4c** and **4d** were prepared by heating the neat reactants for 2 h using an oil bath maintained at 75 °C and 105 °C, respectively.

Because ylides and their precursors are sensitive to air and moisture, care was exercised in drying tetrahydrofuran, the hydrocarbon and other solvents, and in using dry, air-free equipment with an atmosphere of nitrogen. Rigorous safety precautions were adhered to while handling benzene and the arsenic compounds.

Synthesis and characterization of ylides 3 and 6

Ylide 3a. Phenacyltriphenylphosphonium bromide (**1a**; 12.0 g, 26 mmol) was mixed with sodium hydroxide (1.2 g, 30 mmol), and the reaction mixture was extracted twice with dichloromethane (50 mL). The extract was dried, the solvent was evaporated, and the residue was recrystallized from ethyl acetate to give 1-phenyl-2-(triphenylphosphoranylidene)ethanone **3a** (5.53 g, 56%).[10]

Ylides 3b,**c,f** and **6c.** A suspension of the quaternary phosphonium salt (12.5 mmol), i.e., phenacyltriphenylphosphonium bromide (**1b**, 5.76 g), benzyltriphenylphosphonium bromide (**1c**, 5.40 g), propyltriphenylphosphonium bromide (**1f**, 4.81 g), or quaternary arsonium salt (12.5 mmol), i.e., benzyltriphenylarsonium bromide (**4c**, 5.96 g) in dry THF (60 mL) was stirred at room temperature under a nitrogen atmosphere, while a solution of 1.6 M butyllithium in dry hexane (0.83 g, 13 mmol) was slowly added with a syringe. The mixture was stirred for 1–3 h, then a solution of benzoyl bromide (1.16 g, 6.25 mmol) in dry THF (10 mL) was added dropwise to the solution and the reaction mixture was stirred overnight. The mixture was filtered, and the filtrate was evaporated. The residue was dissolved in dichloromethane (150 mL), dried and the solvent was evaporated. The residue was recrystallized from ethyl acetate to give crystalline ylides **3b** (1.39 g, 46%), **3c** (1.91 g, 67%), **3f (**1.20 g, 47%). The oily residue from the reaction of **4c** was dissolved in chloroform (50 mL), and the solution was extracted twice with water (100 mL). The chloroform layer was separated and dried, and the residual oil was crystallized. The solid obtained was recrystallized from dichloromethane/hexane (1:1) to give **6c** (1.70 g, 21%).[1, 2]

Ylides 3d, 6d. To an ice-cold solution of ethoxycarbonylmethyltriphenylphosphonium bromide (**1c**, 2.27 g, 5.53 mmol) or ethoxycarbonylmethyltriphenylarsonium bromide (**4c**, 2.51 g, 5.3 mmol) in dry toluene was added triethylamine (1.11 g, 11 mmol). The mixture was stirred for 30 min, and a solution of benzoyl chloride (0.75 g, 5.3 mmol) in anhydrous chloroform (5 mL) was then added dropwise. The mixture was stirred at 0 °C for 30 min, and was then kept at room temperature for 24 h. The reaction mixture was finally washed with water (2×50 mL), the chloroform layer was separated, dried, evaporated, and the residue was crystallized from benzene/cyclohexane 1:1 by allowing the hot solution to cool gradually to give ethyl 3-oxo-3-phenyl-2-(triphenylphosphoranylidene)propanoate **3d** (1.20 g, 50%) and ethyl 3-oxo-3-phenyl-2-(triphenylarsonylidene)propanoate **6d** (1.4 g, 55%), respectively.[18, 21]

Ylide 3e. Ylide **3a** (5.0 g, 1.3 mmol) was mixed with triethylamine (1.62 g, 1.6 mmol), and the mixture was stirred in dry THF (75 mL) at room temperature for 2 h. Benzenesulfonyl chloride (2.3 g, 1.3 mmol) was then added dropwise while keeping the reaction mixture at 50 °C. After the addition was completed, stirring was continued overnight at room temperature. The reaction mixture was then washed with water (3×50 mL), dried and evaporated. The residual oil was subjected to column chromatography on silica gel using diethyl ether/petroleum ether (40–60 °C) 3:2 as eluent, and the solid residue obtained was recrystallized from ethyl acetate to give 1-phenyl-2-(phenylthio)-2-(triphenylphosphoranylidene)ethanone **3e** (0.64 g, 10%).

Ylide 6a. A slurry of 50% sodium hydride (5 g) in mineral oil was added to a slurry of phenylacyltriphenylarsonium bromide (**4a**; 11.0 g, 22 mmol) in dry benzene (100 mL) containing absolute alcohol (0.5 mL), and the reaction mixture was stirred overnight. The mixture was then filtered, and the filtrate was diluted with hexane. The precipitate thus obtained was collected and recrystallized from the benzene/hexane (1:1) to give 1-phenyl-2-(triphenylarsoranylidene)-ethanone **6a** (9.05 g, 97%).[7]

Ylide 6b. Ylide **6a** (0.85 g, 2 mmol) was mixed with benzoic anhydride (0.45 g, 2 mmol) in benzene (20 mL), and the mixture was stirred overnight. The oil recovered after evaporation of the solvent was triturated with ether, and recrystallized from the benzene/hepatane to give 1,3-diphenyl-2-(triphenylarsoranylidene)propan-1,3-dione **6b** (0.52 g, 49%).[7]

1-Phenyl-2-(triphenylphosphoranylidene)ethanone (3a). Colorless crystals (5.53 g, 56%); mp 180-182 °C; IR (KBr): $\tilde{\nu}$1587, 1525, 1483, 1438, 1386, 1300, 1184, 1104, 1052, 890, 873, 712, 514 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.46 (d, J = 24 Hz, 1H), 7.37 (t, J = 3 Hz, 3H), 7.48–7.51 (m, 6H), 7.56–7.60 (m, 3H), 7.72–7.77 (m, 6H), 7.99–8.01 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 51.29 (d, J_{P-C} = 111.4 Hz, P=C), 127.52, 127.66 (d, J_{P-C} = 90.6 Hz, C-1 of P-Ph), 128.34, 129.48 (d, J_{P-C} = 12 Hz, C-3 of P-Ph), 129.96 (2C), 132.65 (d, J_{P-C} = 2.7 Hz, C-4 of P-Ph), 133.75 (d, J_{P-C} = 10 Hz, C-2 of P-Ph), 141.84(d, J_{P-C} = 14.5 Hz) 185.48 (d, J_{P-C} = 3.3 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ 17.84. Anal. calcd. for $C_{26}H_{21}OP$: C, 82.10; H, 5.52. Found: C, 81.61; H, 5.58.

1,3-Diphenyl-2-(triphenylphosphoranylidene)propan-1,3-dione (3b). White crystals (1.39 g, 46%); mp 160–162C. ^1H NMR ($CDCl_3$): δ 7.00–7.09 (m, 6H), 7.45–7.53 (m, 10H), 7.56–7.59 (m, 3H), 7.767.81 (m, 6H). Anal. calcd. for $C_{33}H_{25}O_2P$: C, 81.82; H, 5.17. Found: C, 81.58; H, 5.14.

1,2-Diphenyl-2-(triphenylphosphoranylidene)ethanone (3c). White crystals (1.91 g, 67%); mp 130–132 °C. ^1H NMR ($CDCl_3$): δ 7.43–7.58 (m, 15H), 7.64–7.72 (m, 10H). Anal. calcd. for $C_{32}H_{25}OP$: C, 84.21; H, 5.48. Found: C, 83.96; H, 5.29.

Ethyl 3-oxo-3-phenyl-2-(triphenylphosphoranylidene)propanoate (3d). White crystals (1.20 g, 50%); mp 174–175 °C. ^1H NMR ($CDCl_3$): δ 0.82 (t, J = 7 Hz, 3H), 3.90 (q, J = 7 Hz, 2H), 7.25–7.85 (m, 20H); ^{31}P NMR ($CDCl_3$): δ 17.5. Anal. calcd. for $C_{29}H_{25}O_3P$**:** C, 76.99; H, 5.53. Found: C, 76.80; H, 5.41.

1-Phenyl-2-(phenylthio)-2-(triphenylphosphoranylidene)ethanone (3e). White crystals (0.64 g, 10%); mp 217-219 °C. IR (KBr): $\tilde{\nu}$ 3050, 1580, 1509, 1435, 1338, 1306, 1104, 996,

713, 686 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.02 (t, J = 8 Hz, 1H), 7.14 (t, J = 8 Hz, 2H), 7.21 (d, J = 8 Hz, 2H), 7.30–7.39 (m, 2H), 7.40–7.44 (m, 6H), 7.51–7.55 (m, 4H), 7.59–7.64 (m, 6H), 7.81 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 57.30 (d, $J_{P,C}$ = 101 Hz, C=P), 124.65, 125.16, 126.95 (d, $J_{P,C}$ = 90 Hz,1-C_{Ph-P}), 127.80, 128.52, 128.69, 128.83 (d, $J_{P,C}$ = 12 Hz, 3-C_{Ph-P}), 129.70, 132.25 (d, $J_{P,C}$ = 3 Hz, 4-C_{Ph-P}), 134.15 (d, $J_{P,C}$ = 10 Hz, 2-C_{Ph-P}), 141.13 (d, $J_{P,C}$ = 11 Hz), 144.47 (d, $J_{P,C}$ = 2 Hz), 192.77 (d, $J_{P,C}$ = 13 Hz, C=O). ^{31}P NMR ($CDCl_3$): δ 27.16. Anal. calcd. for $C_{32}H_{25}OPS$: C, 78.69; H, 5.13; S, 6.55. Found: C, 78.64; H, 5.19; S, 6.15. X-ray analysis verified the structure of **3e**. X-ray data for compound **3e** (Ref. CCDC 665013) are obtainable from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEW, England, UK.

1-Phenyl-2-(triphenylphosphoranylidene)butan-1-one (3f). Colorless crystals **(**1.20 g, 47%); mp 197–200 °C. IR (KBr): $\tilde{\nu}$ 1500, 1476, 1436, 1385 1143, 1102, 1019, 745, 705, 687, 525, 512 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.71 (t, J = 7 Hz, 3H), 2.13 (dq, J = 7.2, 22 Hz, 2H), 7.32–7.38 (m, 3H), 7.46–7.50 (m, 6H), 7.53–7.57 (m, 3H), 7.61–7.63 (m, 2H), 7.69–7.74 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 19.35 (CH_3), 21.45 (d, J_{P-C} = 13 Hz, CH_2), 69.43 (d, J_{P-C} = 100Hz, P=C), 127.74 (2C of COPh), 127.93 (d, J_{P-C} = 90 Hz, C-1 of P-Ph), 128.09 (2C of COPh), 128.24 (C-4 of COPh), 128.86 (d, J_{P-C} = 12 Hz, C-3 of P-Ph), 131.86 (d, J_{P-C} = 3Hz, C-4 of P-Ph), 133.89 (d, J_{P-C} = 10 Hz, C-2 of P-Ph), 143.44 (d, J_{P-C} = 13 Hz, C-1 of COPh) and 186.81 (d, J_{P-C} = 5 Hz, CO). ^{31}P NMR ($CDCl_3$): δ 17.40. Anal. calcd. for $C_{28}H_{25}OP$: C 82.35; H, 6.13. Found: C, 82.56; H, 6.17.

1-Phenyl-2-(triphenylarsoranylidene)ethanone (6a). Fine yellow crystals (9.00 g, 97%); mp 174–176 °C. IR (KBr): $\tilde{\nu}$ 1584, 1505, 1483, 1438, 1383, 1081, 742, 705, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.75 (s, 1H, CH), 7.37–7.38 (m, 3H), 7.49–7.59 (m, 9H), 7.73–7.75 (m, 6H), 8.00–8.02 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 57.63 (As=C), 127.64, 128.38, 130.11, 132.07, 132.38, 133.08, 134.31, 140.81, 182.64 (C=O). Anal. calcd. for $C_{26}H_{21}AsO$: C, 73.58; H, 4.95. Found: C, 73.54; H, 4.93.

1,3-Diphenyl-2-(triphenylarsoranylidene)propan-1,3-dione (6b). White crystals (0.52 g, 49%); mp 212–214 °C. IR (KBr): $\tilde{\nu}$ 1704, 1671, 1588, 1573, 1510, 1440, 1354, 1318, 1083, 868, 745, 719, 691, 652 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.98–7.01 (m, 4H), 7.04–7.08 (m, 2H), 7.39-7.45 (m, 4H), 7.50–7.59 (m, 9H), 7.73–7.75 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 93.42, 127.80, 129.68, 129.80, 129.90, 129.99, 132.10, 133.25, 142.44, 191.61 (C=O). Anal. calcd. for $C_{33}H_{25}AsO_2$: C, 75.00; H, 4.73. Found C, 75.10; H, 4.79.

1,2-Diphenyl-2-(triphenylarsoranylidene)ethanone (6c). Pale yellow needles (1.70 g, 21%); mp 160–163 °C. IR (KBr): $\tilde{\nu}$ 1582, 1503, 1476, 1437, 1081, 742, 705 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.94 (s, 5H), 7.15–7.20 (m, 3H), 7.40 (t, J = 7.5 Hz, 6H), 7.50 (t, J = 7.4 Hz, 3H), 7.56 (d, J = 7Hz, 2H), 7.62 (d, J = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 83.55 (As=C), 125.52, 127.79, 127.79, 128.18, 128.74, 129.71, 130.23, 131.70, 133.43, 134.78, 137.99, 140.99, 179.31 (C=O). Anal. calcd. for $C_{32}H_{25}AsO$: C, 76.80; H, 5.00. Found C, 76.50; H, 5.10.

Ethyl 3-oxo-3-phenyl-2-(triphenylarsoranylidene)propanoate (6d). Pale yellow crystals (1.40 g, 53%); mp 144–146 °C. IR (KBr): $\tilde{\nu}$ 1649, 1529, 1507, 1483, 1439, 1371, 1344, 1290,

1253, 1084, 1054, 745, 739, 691 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.50 (t, *J* = 7 Hz, 3H, CH_3), 3.72 (q, *J* =7 Hz, 2H, CH_2), 7.36–7.38 (m, 3H), 7.49–7.56 (m, 9H), 7.72 (d, *J* = 7 Hz, 8H). ^{13}C NMR ($CDCl_3$): δ 14.22, 59.01, 77.10, 127.74, 129.13, 129.73, 129.84, 129.93, 132.05, 133.05, 142.71, 167.30, 191.85. Anal. calcd. for $C_{29}H_{25}AsO_3$: C, 70.16; H, 5.04. Found: C, 70.15; H, 5.08.

Pyrolysates and elimination fragments

Triphenylphosphine oxide (from **3a–f**)**.** ^1H NMR ($CDCl_3$): δ 7.46-7.49 (m, 6H), 7.53–7.56 (m, 3H), 7.66–7.71 (m, 6H). ^{31}P NMR ($CDCl_3$): δ 30.42. MS: *m*/*z* (%) 279 (15), 278 (62, M^+), 277 (100), 265 (39), 264 (15), 263 (13), 262 (18), 201 (29), 152 (17).[22, 23]

Triphenylarsine oxide (from **6b–d**)**.** ^1H NMR ($CDCl_3$): δ 7.53 (t, *J* = 7.6 Hz, 6H), 7.60 (t, *J* = 7.4Hz, 3H), 7.73 (d, *J* = 6.9 Hz, 6H). MS: *m*/*z* (%) 322 (88, M^+), 229 (44), 227 (46), 252 (100).

Triphenylarsine (from **6a**). ^1H NMR ($CDCl_3$): δ 7.39 (s, 15H). ^{13}C NMR ($CDCl_3$): δ 128.94, 129.08, 129.28, 134.37, 140.23. MS: *m*/*z* (%) (100, M^+), 229 (32), 227 (84), 152 (80).[22, 23]

1,3-Diphenylprop-2-yne-1-one (from **3b**, **6b**). IR ($CDCl_3$): $\tilde{\nu}$ 3058, 2198, 1640, 1437, 721, 695 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.41 (m, 2H), 7.48 (m, 1H), 7.52 (m, 2H), 7.62 (m, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 87.30, 93.56, 120.52, 129.07, 129.13, 130.00, 131.25, 133.51, 134.58, 137.28, 178.48. MS: *m*/*z* (%) 206. (75, M^+), 178 (95), 129 (100), 105 (60).[24-26]

2-Phenylsulfanyl-1-phenylethyne (from **3e**). IR ($CDCl_3$): $\tilde{\nu}$ 3059, 2926, 2173 (C≡C), 1559, 1541, 1478 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25–7.29 (m, 1H), 7.38–7.40 (m, 5H), 7.52–7.62 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 75.84, 98.36, 123.36, 126.61, 127.00, 128.79, 128.89, 129.71, 132.04, 133.36. MS: *m*/*z* (%) 211 (16), 210 (100, M^+), 178 (46), 165 (40).[27-29]

1-Phenyl-1-butyne (from **3f**). ^1H NMR ($CDCl_3$): δ 1.27 (t, *J* = 7.4 Hz, 3H), 2.45 (q, *J* = 7.4 Hz, 2H), 7.29–7.30 (m, 2H), 7.42–7.44 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 13.15, 14.35, 80.29, 92.08, 124.44, 127.90, 128.60 (2C), 131.94 (2C). MS: *m*/*z* (%) 130 (76, M^+), 129 (74), 115 (60), 102 (24).[23]

Acetophenone (from **6a**). IR ($CDCl_3$): $\tilde{\nu}$ 3056, 2932, 1706, 1493, 1445, 1263, 1071, 754, 693, 597 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.64 (s, 3H, CH_3), 7.60 (t, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 2H), 7.98 (d, *J* = 7 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 27.05, 128.87, 129.06, 134.13, 137.51, 198.71. MS: *m*/*z* (%) 120 (10, M^+), 119 (36), 105 (50).[22, 23]

Deoxybenzoin (from **6c**). ^1H NMR ($CDCl_3$): δ 8.01 (dd, *J* = 6.5, 1.1 Hz, 2H), 7.48 (m, 3H), 7.28 (m, 5H), 4.28 (s, 2H). MS: *m*/*z* (%) 197 (10), 196 (27, M^+), 105 (100), 91 (21), 77 (60).

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