Synthesis of novel sulfonyl-stabilized phosphorus ylides, and the kinetics and mechanism of their conventional and flash vacuum pyrolysis reactions[1]

Rasha F. Al-Bashir, Nouria A. Al-Awadi, and Osman M.E. El-Dusouqui

Abstract: Nine substituted sulfonyl-stabilized phosphorus ylides were prepared by treating their intermediate ylide analogues with phenylmethanesulfonyl fluoride. The stoichiometric ratio of the reactants for each preparation needed to be adjusted according to the basicity of each ylide intermediate. The nine ylide compounds were then subjected to conventional (sealed-tube) gas-phase pyrolysis at 470–545 K. The pyrolytic reactions were homogeneous and obeyed a first-order rate equation. The values of the Arrhenius log *A* (s^{-1}) and E_a (kJ mol^{-1}) obtained for these reactions averaged 11.12 ± 2.00 and 131.8 ± 24.4, respectively. Analysis of the pyrolysates from conventional pyrolysis and from flash vacuum pyrolysis at 600 K showed the products to be complex mixtures of triphenylphosphine, triphenylphosphine oxide, triphenylphosphine sulfide, and symmetric and unsymmetric alkenes. Conventional pyrolysis also gave novel mixed sulfones and, for the *p*-methoxyaryl substituent, *p*-anisaldehyde. The products of the reactions under study are explained on the basis of a mechanism involving a sulfonyl carbene intermediate, and the reaction mechanism is used to rationalize the kinetic results and molecular reactivities.

Key words: ylides, synthesis, pyrolysis, kinetics, mechanism.

Résumé : La réaction d'analogues d'ylures intermédiaires avec le fluorure de phénylméthanesulfonyle a permis de préparer neuf ylures de phosphores substitués, stabilisés par un groupe sulfonyle. Le rapport stoechiométrique des réactifs nécessaires pour chacune des préparations a été ajusté en fonction de la basicité de chaque ylure intermédiaire. On a ensuite soumis chacun des neuf ylures à une pyrolyse à phase gazeuse, en tube scellé, à des températures allant de 470 à 545 K. Les réactions pyrolytiques sont homogènes et obéissent à une équation de vitesse du premier ordre. Les valeurs moyennes pour les paramètres d'Arrhenius, log *A* (s^{-1}) et E_a (kJ mol^{-1}), obtenues pour ces réactions sont respectivement de 11,12 ± 2,00 et de 131,8 ± 24,4. L'analyse des produits de pyrolyse conventionnelle et de pyrolyse éclair sous vide à 600 K montrent que les produits correspondent à des mélanges complexes comprenant de la triphénylphosphine, de l'oxyde de triphénylphosphine, de sulfure de triphénylphosphine ainsi que des alcènes symétriques et non symétriques. La pyrolyse conventionnelle conduit aussi à de nouvelles sulfones mixtes et, dans le cas du substituant *p*-méthoxyaryle, à du *p*-anisaldéhyde. Les produits des réactions obtenus dans cette étude sont expliqués sur la base d'un mécanisme impliquant un intermédiaire sulfonylcarbène et on utilise le mécanisme réactionnel pour rationaliser les résultats cinétiques et les réactivités molaires.

Mots clés : ylures, synthèse, pyrolyse, cinétique, mécanisme.

[Traduit par la Rédaction]

Introduction

Reports on the synthesis of sulfonyl-stabilized phosphorus ylides suggest two formal steps in the preparation: first, a base, butyl lithium (BuLi), reacts with the appropriate quaternary phosphonium halide salt (QS) in a nitrogen atmosphere to give an intermediate ylide, which then proceeds to react with the designated sulfonyl fluoride (RSO_2F) to form the target ylide (1–4). In the present study, this procedure was found, however, not to be uniform and straightforward, as the stoichiometric ratio of the reactants (QS:BuLi:RSO_2F) needed to be adjusted according to the basic strength of the ylide intermediate formed in the first step. Besides, it has been noted that α-sulfonyl ylides cannot be prepared by treatment of the intermediate ylides with sulfonyl chloride derivatives, since this procedure results in the formation of α-chloro ylides instead of the target sulfonyl-stabilized phosphorus ylides (4). Hence, sulfonyl fluorides were used instead.

Aitken et al. (1) have shown that flash vacuum pyrolysis at 600 K of sulfonyl-stabilized phosphorus ylides gave Ph_3P, Ph_3PO, Ph_3PS, and alkenes (either symmetric or unsymmetric). These products are consistent with the formation of

Received 9 May 1005. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 25 November 2005.

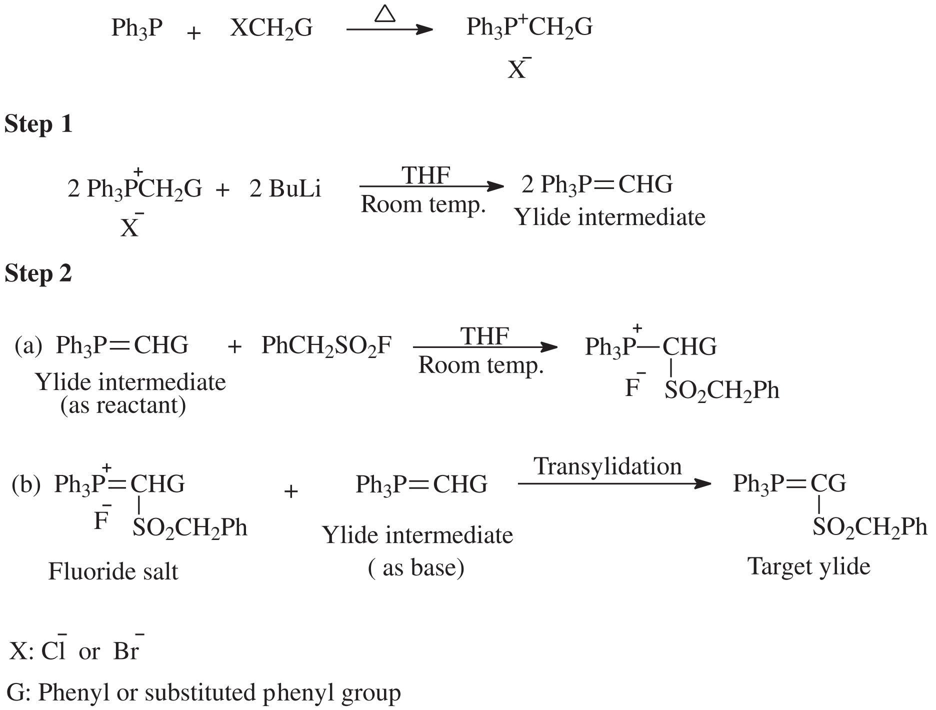
R.F. Al-Bashir, N.A. Al-Awadi,[2] and O.M.E. El-Dusouqui. Department of Chemistry, University of Kuwait, P.O. Box 5969, Safat 13060, Kuwait.

[1] This article is part of a Special Issue dedicated to organic reaction mechanisms.

[2] Corresponding author (e-mail: nouria@kuc01.kuniv.edu.kw).

Can. J. Chem. **83**: 1543–1553 (2005) doi: 10.1139/V05-210

Scheme 1. Reaction pathway for ylides **3**–**9**.



a sulfonyl carbene intermediate. The phosphorus oxides and sulfides can be accounted for by the separate extrusion of Ph_3P and SO_2, which then partly combine to give Ph_3PO and Ph_3PS, and the validity of this was confirmed by control experiments (1). The sulfonyl-stabilized ylides were obtained as stable, high-melting solids with characteristic spectral data including diagnostic ^{31}P NMR signals at δ 16.9–21.7 ppm. Here, we report the results of a study on the kinetics and reaction product of thermolysis of nine substituted sulfonyl-stabilized phosphorus ylides using conventional (sealed-tube (ST); static) pyrolysis (CP), and compare the products of reaction with those from flash vacuum pyrolysis (FVP). The kinetic investigation also provides a novel insight into molecular reactivities and the effects of substituents on the pyrolysis of stabilized phosphorus ylides.

The nine ylide compounds under study are derivatives of [(benzylsulfonyl)methylene](triphenyl)phosphorane ($Ph_3P=C(G)SO_2CH_2Ph$) in which the substituent (G) is: *p*-CNC_6H_4 (**1**), *p*-$NO_2C_6H_4$ (**2**), *m*-$NO_2C_6H_4$ (**3**), *p*-ClC_6H_4 (**4**), *m*-ClC_6H_4 (**5**), C_6H_5 (**6**), *p*-$CH_3C_6H_4$ (**7**), *p*-$CH_3OC_6H_4$ (**8**), and CH_3 (**9**), respectively.

Results and discussion

Synthesis

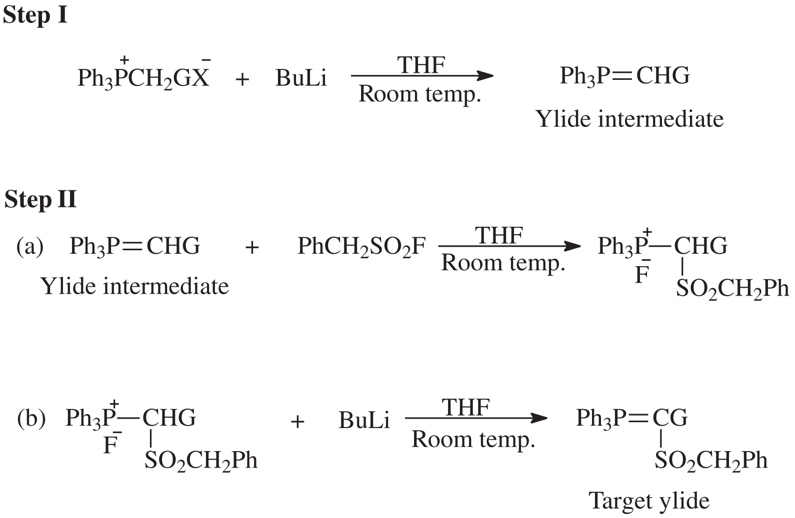
Synthesis of ylides **3**–**9** according to literature procedures (1) required the ratio of the reactants, quaternary phosphonium halide salt ($Ph_3P^+CH_2GX^-$) : BuLi : phenylmethanesulfonyl fluoride ($PhCH_2SO_2F$), to be 2:2:1; as these reactions involve transylidation to regenerate one molecule of quaternary phosphonium fluoride salt (Scheme 1). In these cases, the basicity of the ylide intermediate formed in step 1 is high enough for it to act also as the base needed to abstract the proton from the quaternary phosphonium salt formed in step 2*a* to give the target ylide in transylidation step 2*b*. The electron-withdrawing substituents (CN and *p*-NO_2) of the phenyl group in ylides **1** and **2**, respectively, will decrease the protophilic character of the multiple bond of these ylides relative to that of ylides **3**–**9**, and so the amount of BuLi base had to be doubled to avoid formation of excess ylide intermediate and to provide the base required in step 2*b* (Scheme 2). Accordingly, the reactant ratio of quaternary phosphonium halide salt : BuLi : phenylmethanesulfonyl fluoride was adjusted to 1:2:1.

Attempts to synthesize ylide **1** (G = *p*-CNC_6H_4) using the ratio of 2:2:1 failed to give any ylide product. Besides, it is of interest to note that the reactant ratio of 1:2:1, which gave ylide **2** (G = *p*-$NO_2C_6H_4$) in 72% yield, failed to give ylide **3** (G = *m*-$NO_2C_6H_4$), which, however, was obtained in 65% yield when the reactant ratio of 2:2:1 was used instead; this same ratio was also used for ylides **3**–**9**. The present findings indicate that the basicity of the ylide intermediate obtained in the initial step of the reaction determines whether the intermediate ylide is basic enough to act as the proton scavenger in the transylidation reaction, or that the stronger BuLi base is needed to complete the reaction. The stoichiomeric ratio of the reactants as well as the % yield of the target ylides correlate well with the expected relative basicities of the intermediate ylides as judged by the electron-donating and electron-withdrawing effect of the group in substituent G.

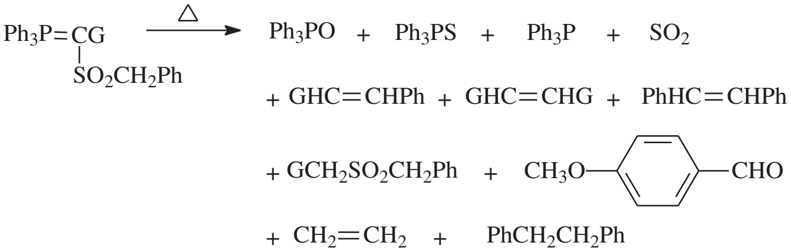
Pyrolysates and reaction mechanism

Reaction products for complete pyrolysis were obtained for all nine substrates (*i*) in a FVP (flow) reactor at 600 K, and (*ii*) in a sealed-tube pyrolyser (static method) at temperatures exceeding those used in the kinetic investigations. The static-method reactions (CP reaction) were allowed ample residence time to ensure maximum pyrolysis. The constituents of the pyrolysates obtained by this method were isolated

Scheme 2. Reaction pathway for ylides **1** and **2**.



Scheme 3. Composition of the products of gas-phase pyrolysis of ylides **1**–**9**.



using preparative liquid chromatography (PLC) and analyzed using GC–MS, FT-IR, and ^{1}H NMR techniques. The pyrolysates from FVP were collected in a cold trap. FVP and CP gave identical products of Ph_3P, Ph_3PO, Ph_3PS, and alkenes (symmetric and unsymmetric) (Scheme 3). However, static pyrolysis of the ylides followed by PLC gave better separation and isolation profiles of alkenes, and allowed the identification of more reaction products, including *p*-anisaldehyde and mixed sulfones, which were not detected in the pyrolysates from FVP. It is noteworthy that the static (sealed-tube) method provides longer residence time for novel pyrolytic reaction pathways. Identification and characterization of the constituents of the pyrolysates are detailed in the Experimental section.

[(Benzylsulfonyl)(4-cyanophenyl)methylene](triphenyl)phosphorane (ylide 1)

The analysis of the pyrolysates — separated as oils — showed 4-cynostilbene, which was separated in pure form on PLC. *trans*-Stilbene and novel *trans*-4,4′-dicyanostilbene were also isolated in a very pure state as well from a separate fraction. In a third fraction, (4-cyanobenzyl)benzyl sulfone identified for the first time in the present study, was isolated as a novel sulfone only by CP.

[(Benzylsulfonyl)(4-nitrophenyl)methylene](triphenyl)phosphorane (ylide 2)

Analysis by ^{1}H NMR, IR, and MS showed a mixture of alkenes, namely, *trans*-4-nitrostilbene and *trans*-stilbene, both clearly identified. A major fraction, novel (4-nitrobenzyl)benzylsulfone, isolated by CP only, was properly characterized and identified.

[(Benzylsulfonyl)(3-nitrophenyl)methylene](triphenyl)phosphorane (ylide 3)

The analysis of the products of reaction of this ylide showed a mixture of two alkenes: *trans*-3-nitrostilbene (major fraction) and *trans*-stilbene; the latter identified only through the static method. Besides, (3-nitrobenzyl)benzyl sulfone was isolated and clearly identified as a novel compound using the static pyrolysis technique.

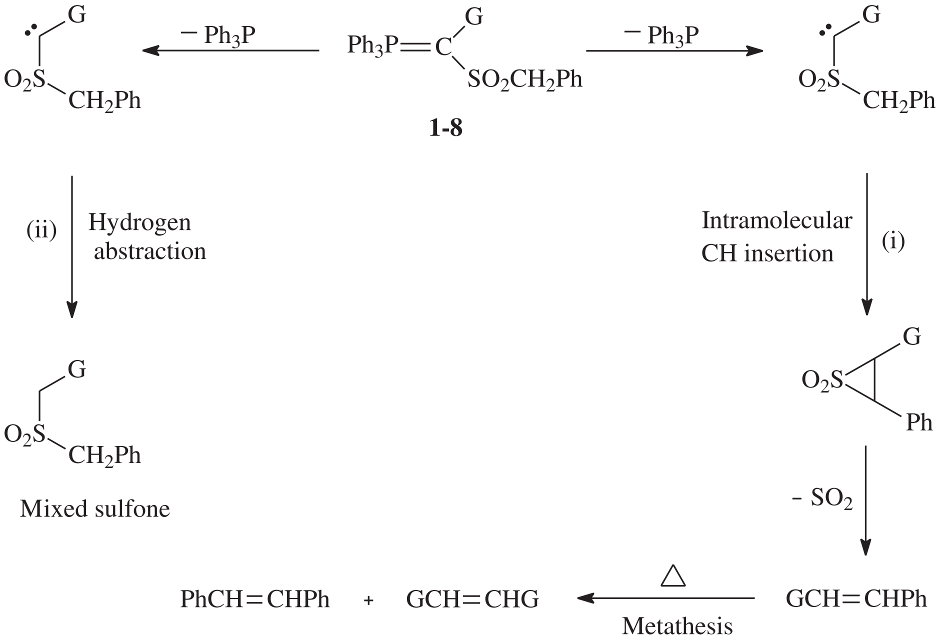
[(Benzylsulfonyl)(4-chlorophenyl)methylene](triphenyl)phosphorane (ylide 4)

The spectral analysis (^{1}H NMR, IR, and MS) of the products proved the presence of 4,4′-dichlorostilbene, which was separated in a pure form by PLC. Both *trans*-4-chlorostilbene and *trans*-stilbene were present as well in small amounts. The ^{1}H NMR for *trans*-4-chlorostilbene in $CDCl_3$ showed signals (5) at δ 6.83 (1H, d, J = 16.4 Hz), 6.91 (1H, d, J = 16.4 Hz), 7.07–7.42 (9H, m). MS *m*/*z*: 216 (34% abundance) molecular ion, 215 (17%), 214 (100%) base peak, 179 (45%), 178 (59%). Novel (4-chlorobenzyl)benzyl sulfone obtained by the static technique was separated as a pure fraction on PLC.

[(Benzylsulfonyl)(3-chlorophenyl)methylene](triphenyl)phosphorane (ylide 5)

Reaction product separation on PLC showed 3-chlorostilbene, 3,3′-dichlorostilbene, and *trans*-stilbene. ^{1}H

Scheme 4. Generation and further reaction of the sulfonyl carbene intermediate of ylides **1**–**8**.



NMR for *trans*-3,3′-dichlorostilbene in $CDCl_3$ showed diagnostic signals (6) at δ 7.03 (2H, s), 7.32–7.42 (8H, m), and for *trans*-3-chlorostilbene (7) at δ 6.85 (1H, d, *J* = 16.5 Hz), 6.92 (1H, d, *J* = 16.5 Hz), 7.11–7.42 (9H, m). (3-Chlorobenzyl)benzyl sulfone was also isolated for the first time in this study using CP.

It is to be noted that FVP does not give the sulfone products.

Ylides 6, 7, and 9

The FVP at 600 K of these ylides has been studied before (1). In each case a mixture of Ph_3P, Ph_3PO, and Ph_3PS was produced together with various alkenes, exactly as observed in the present study for ylides **1**–**5**. Static pyrolysis of these ylides gave products identical to those obtained through FVP.

[(Benzylsulfonyl)(4-methoxyphenyl)methylene](triphenyl)-phosphorane (ylide 8)

The spectral analysis of the products by both FVP and the static method showed *trans*-methoxystilbene; δ_H ($CDCl_3$) (6): 4.01 (3H, s), 6.88 (2H, d, *J* = 8.5 Hz), 6.98 (1H, d, *J* = 16.3 Hz), 7.08 (1H, d, *J* = 16.3 Hz), 7.10–7.55 (m, 7H). MS *m*/*z*: 210 ($M^{+\cdot}$, 22% abundance) molecular ion, 209 (100%) base peak, and fragment ions at 194 (12%), 195 (6%), 165 (33%), 166 (10%), 152 (6%), 135 (16%), 121 (33%).

In a separate fraction, *trans*-4,4′-dimethoxystilbene was identified; δ_H ($CDCl_3$) (8): 3.86 (6H, s), 6.91 (4H, d, *J* = 6.85 Hz), 6.95 (2H, s), 7.45 (4H, d, *J* = 6.85 Hz). MS *m*/*z*: 240 ($M^{+\cdot}$, 100%), molecular ion and base peak, fragment ions (9) at 226 (18%), 225 (49%), 165 (45%), 153 (28%), 152 (32%), 120 (12%). Besides, *trans*-stilbene was also isolated in a third fraction, but the sulfone fraction could not be identified even on using CP. Instead, 4-methoxybenzyaldehyde (*p*-anisaldehyde) was isolated in a very pure state.

According to these results, the composition of the products of the gas-phase pyrolysis of the substituted sulfonyl-stabilized ylides (**1**–**9**) was as shown in Scheme 3. Based on the overall pyrolysate composition, a feasible reaction mechanism is proposed to account for the product of the gas-phase pyrolytic reaction of the sulfonyl-stabilized phosphorus ylides (**1**–**9**) under study. The mechanism involves the formation and further reaction of a sulfonyl carbene intermediate (1).

In the case of ylides **1**–**8** (Scheme 4): (*i*) The carbene intermediate obtained reacts by an intramolecular CH insertion process to give thiirane dioxide, followed by loss of SO_2, alkene metathesis, and the partial reaction of Ph_3P with SO_2 to give Ph_3PO and Ph_3PS; (*ii*) the carbene intermediate abstracts hydrogen in a novel reaction, observed only in pyrolysis by the static method of ylides **1**–**5** (all with an electron-withdrawing group in substituent G), to give mixed sulfones (Scheme 4). It is to be noted that for ylide **6** (G = Ph) and ylides **7** and **8** (electron-donating groups in G) no such sulfone products were detected in the pyrolysates. The formation of 4-methoxybenzaldehyde (*p*-anisaldehyde) by ylide **8** involves a novel route in which the carbene centre seems to abstract O and H possibly through a free radical pathway to give the aldehyde. An earlier study on the pyrolysis of arylsulphonyl-stabilized phosphorus ylides reports aldehyde formation for substrates in which the aryl substituent is an *o*-methoxyphenyl group (1).

When G = CH_3 (ylide **9**), literature reports (1, 3) suggest two pathways (Scheme 5) for the reaction of the sulfonyl carbene intermediates.

Kinetic analysis

The kinetic data of the pyrolytic gas-phase elimination reactions of the nine ylides (**1**–**9**) under study are given in Table 1. Each rate constant at any given temperature represents an average from a set of three values obtained in three separate kinetic runs conducted at the same temperature. The agreement among the values of the rate constant in each set is within ±2%. Each kinetic run was monitored until 90%–95% of the reaction was completed, and the range of 44 ±

Scheme 5. Reaction pathway of ylide **9**.

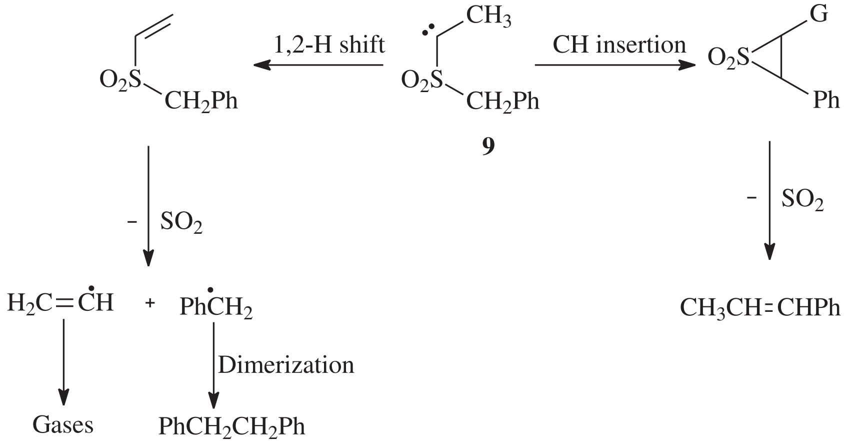


Table 1. Rate constants (k, s^{-1}), Arrhenius log A and E_a, entropies of activation ($\Delta S^{\ddagger}$), and rate constants at 500 K of the gas-phase pyrolysis of sulfonyl-stabilized phosphorus ylides (**1**–**9**).

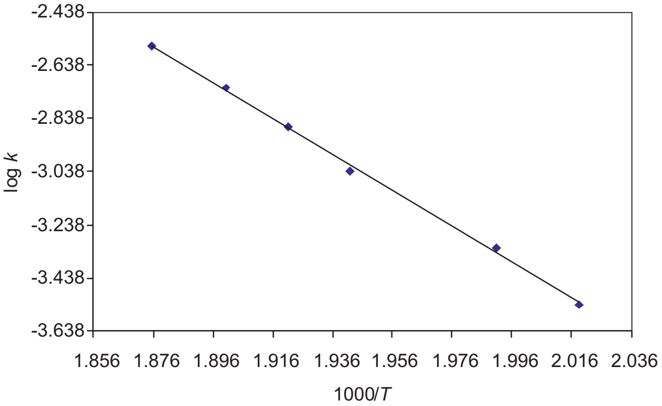
Ylide	G	T (K)	10^4k (s^{-1})	log A (s^{-1})	E_a (kJ mol^{-1})	$10^4k_{500\ K}$ (s^{-1})	$\Delta S^{\ddagger}_{500\ K}$ (J K^{-1} mol^{-1})
1	p-CNC_6H_4	495.4	2.899	10.11±0.26	129.4±2.51	3.93	–55.62
		502.4	4.737				
		515.0	9.194				
		520.4	13.53				
		526.2	18.87				
		533.2	27.08				
2	p-$NO_2C_6H_4$	487.0	2.368	13.12±0.25	156.1±2.43	6.41	+1.895
		494.8	4.313				
		502.4	8.705				
		509.4	13.19				
		516.6	20.00				
		529.4	53.36				
3	m-$NO_2C_6H_4$	492.4	3.939	8.63±0.08	113.4±0.79	6.11	–84.10
		499.2	5.745				
		507.0	8.680				
		513.8	12.50				
		520.6	17.90				
		527.8	25.72				
		534.8	34.74				
4	p-ClC_6H_4	494.8	2.748	8.65±0.18	115.6±1.84	3.78	–83.64
		502.6	4.502				
		509.7	6.269				
		523.4	13.62				
		538.2	26.17				
		544.8	37.59				
5	m-ClC_6H_4	494.2	2.122	7.67±0.15	107.4±1.55	2.88	–102.3
		506.2	3.942				
		515.6	6.116				
		522.5	9.016				
		530.0	12.92				
		536.2	15.91				
		543.7	22.88				
6	C_6H_5	500.8	5.527	9.75±0.06	124.7±0.63	5.32	–62.61
		508.4	8.917				
		516.2	13.39				
		524.2	21.17				

Table 1 (*concluded*).

Ylide	G	T (K)	10^4k (s^{-1})	log A (s^{-1})	E_a (kJ mol^{-1})	$10^4k_{500\ K}$ (s^{-1})	$\Delta S^{\ddagger}_{500\ K}$ (J K^{-1} mol^{-1})
		531.4	31.64				
		539.0	46.49				
		545.2	63.72				
7	p-$CH_3C_6H_4$	479.2	3.656	9.13±0.14	115.3±1.34	12.0	–74.54
		493.8	8.356				
		501.6	12.74				
		509.4	20.14				
		524.0	43.28				
8	p-$CH_3OC_6H_4$	475.0	2.190	11.53±0.34	134.0±3.26	12.5	–28.53
		483.0	3.882				
		491.6	6.849				
		498.2	10.95				
		505.0	19.03				
		512.2	25.11				
		520.4	47.33				
9	CH_3	470.4	3.194	8.43±0.14	107.4±1.25	16.2×10^{-4}	–87.95
		476.4	4.366				
		483.6	6.871				
		490.4	9.945				
		497.2	14.14				
		504.4	20.54				
		511.8	28.52				

6 K over which the reactions were followed is in accord with the temperature range deemed necessary for reliable kinetic analysis of thermal gas-phase elimination reactions (10, 11). Arrhenius parameters were obtained using the results from Table 1. The Arrhenius plots were linear over the studied temperature and reaction range, with correlation coefficients of the order of 0.990 ± 0.009. A representative plot is given in Fig. 1 for [(benzylsulphonyl)(4-cyanophenyl)methylene](triphenyl)phosphorane (ylide **1**), with a correlation coefficient of 0.999. Arrhenius log A (s^{-1}), $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}), the energy of activation (E_a, kJ mol^{-1}), and the first-order rate constants (k, s^{-1}) of the pyrolysis reactions at 500 K are recorded in Table 1. The values for $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) are negative or small (positive) suggesting higher structural organization and the formation of an ordered transition state.

Fig. 1. Arrhenius plot for the pyrolysis of ylide **1**.



Molecular reactivities and substituent effects

The first-order rate constants at 500 K of the gas-phase pyrolytic reactions of ylides **1–9** and the rate constant ratio (relative rate, k_{rel}) of the ylides are summarized in Table 2.

The main features of the kinetic results are as follows:

1. The rate of pyrolysis of ylide **9**, where G = CH_3, is ca. 3 times faster than the rate of pyrolysis of ylide **6**, where G = C_6H_5; this represents the highiest increment in reactivity in the series of ylides under consideration and is attributed to the fact that the reactive carbene intermediate of ylide **9** can react either by 1,3-H insertion or 1,2-H insertion followed by the elimination of SO_2. The pyrolysates 1-phenylpropene and dibenzyl prove the possibility of both modes of insertion, where G is the aromatic phenyl group, the carbene intermediate can react only by 1,3-insertion.
2. Introducing p-methyl and p-methoxy groups into the aromatic ring ylides **7** and **8** respectively, has increased the rate of pyrolysis by almost 2.3 times for both ylides; this could be explained in terms of the electron-donating nature of these substituents and their influence on the carbene intermediate suggested (Schemes 4 and 5).
3. When electron-withdrawing substituents (p-Cl, m-Cl, and p-CN) were introduced into ylides **4**, **5**, and **7**, respectively, the reactivity was reduced; this indicates that these substituents destabilize the carbene intermediate.
4. Introducing the nitro group at the *para* and *meta* positions of ylides **3** and **4**, respectively, resulted in no change on the reactivity compared to ylide **6** (G = C_6H_5); this unique behaviour of the nitro group in the gas-phase thermal elimination reactions of organic compounds has been reported in other studies (12).

Table 2. Rate constants (k, s^{-1}) at 500 K and the rate constant ratio (relative rate, k_{rel}) of the pyrolysis of sulfonyl-stabilized phosphorus ylides (**1**–**9**).

Ylide	G	$10^4\ k$ (s^{-1})	k_{rel}
1	p-CNC_6H_4	3.926	0.738
2	p-$NO_2C_6H_4$	6.406	1.20
3	m-$NO_2C_6H_4$	6.109	1.15
4	p-ClC_6H_4	3.782	0.711
5	m-ClC_6H_4	2.881	0.542
6	C_6H_5	5.317	1.00
7	p-$CH_3C_6H_4$	12.00	2.26
8	p-$CH_3OC_6H_4$	12.48	2.35
9	CH_3	16.17	3.04

5. It is important to note that these sulfonyl carbene intermediates are already stabilized by conjugative interaction with the sulfonyl group (Scheme 6), and this might be the reason behind the relatively small substituent effects obtained.

These features of the kinetic results support the reaction pathways suggested and that the formation of the carbene intermediate is the rate-controlling step.

Experimental

Materials, techniques, and instrumentation

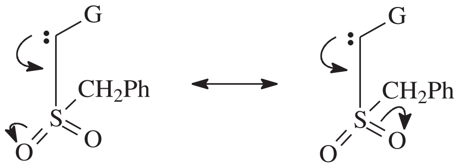
The required quaternary phosphonium salts were prepared by the reaction of the appropriate alkyl halide with triphenylphosphine in boiling toluene. The phenylmethanesulfonyl fluoride, BuLi, and dry THF are commercially available from Aldrich. Further drying of THF was made by distillation from potassium benzophenone ketyl under N_2. The ylides and the constituents of their pyrolysates were characterized using GC–MS, FT-IR, ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. Instrumentation included a Finnigan Mat INCOSXL for GC–MS studies, a PerkinElmer 2000 spectrometer for FT-IR, and a Bruker DPX 400 spectrometer for the NMR analysis. Kinetic runs and pyrolysates preparation for reaction product analysis using a sealed-tube pyrolyser (conventional static pyrolysis) were conducted in a Chemical Data System (CDS) custom-made pyrolyzer comprising an insulated aluminum block fitted with a platinum-resistance thermometer and thermocouple connected to a Comark microprocessor thermometer. The temperature of the aluminum block was controlled by a digital Eurotherm 093 precision temperature regulator. Aluminum was chosen for its low temperature gradient and resistance to elevated temperatures. HPLC analysis of kinetic runs was carried out on a Waters prope (pump model 515 and UV detector model 2487).

FVP was conducted in a fused-quartz tube, which was housed in a sublimation oven. The latter was connected to a hot zone pyrolyzer under low pressure ending with a U-shaped trap cooled in liquid nitrogen.

Synthesis and characterization of ylides (1–9)

The details of the synthesis of the novel sulfonyl-stabilized ylides **1** and **3**–**5** are given in the following, while ylides **2** and **6**–**9** were prepared following literature procedures (1, 3). The general procedure A for the synthesis of ylides **1** and **2**, and procedure B for the preparation of ylides **3**–**9** are described hereafter.

Scheme 6. Carbene intermediate stabilization by conjugative interaction with sulfonyl groups.



Synthesis

Procedure A

In the synthesis of ylides **1** and **2**, a solution of 1.6 mol/L BuLi in hexane (7.5 mmol) was slowly added from a syringe to a stirred suspension of the corresponding quaternary phosphonium salt (7.5 mmol) in dry THF (50 mL) at room temperature under nitrogen. The mixture was stirred for about 1 h, and then an equivalent amount of phenylmethanesulfonyl fluoride (7.5 mmol) in dry THF (ca. 5 mL) was added all at once. The reaction mixture was stirred further for 5 h, followed by the addition of another portion of BuLi in hexane (7.5 mmol). The crude material was dissolved in dichloromethane (100 mL), washed with water (3 × 75 mL), dried, and concentrated under vacuum. The residual oil was triturated with a suitable solvent to obtain the pure ylide.

Procedure B

For the preparation of ylides **3**–**9**, a suspension of the appropriate quaternary phosphonium salt (15 mmol) in dry THF (100 mL) was stirred at room temperature under nitrogen while a solution of 1.6 mol/L BuLi in hexane (15.6 mmol) was slowly added from a syringe. The mixture was stirred further for about 1 h, and then a solution of phenylmethanesulfonyl fluoride (7.5 mmol) in dry THF (10 mL) was added dropwise to the ylide solution. The mixture was kept stirring overnight, and the reaction mixture was then filtered and the filtrate was evaporated. The residue was dissolved in dichloromethane (150 mL) and washed with water (3 × 75 mL), dried and the solvent evaporated (1, 3).

A problem encountered in the preparation of stabilized ylides in general, and in the synthesis of the present ylides, they were often difficult to crystallize in pure form from the oils obtained following the evaporation step. Since the products hydrolyzed when chromatography was attempted, and decomposed on sublimation, the safer option was their trituration with suitable solvents to obtain the pure ylides (13).

Characterization

Ylides **2** and **6**–**9** were gratefully received from Dr. Alan Aitken, University of St. Andrews, St. Andrews, Fife UK. The ylides were purified, recrystallized from dichloromethane–ether (ylide **2**), ethylacetate (ylides **6**–**9**), and characterized before use.

[(Benzylsulfonyl)(4-cyanophenyl)methylene](triphenyl)phosphorane (1)

The quaternary phosphonium salt, 4-cyanobenzyltriphenylphosphonium bromide (**$Ph_3P^+CH_2$*p*-$NCC_6H_4Br^-$**), was prepared by refluxing 10.49 g of triphenylphosphine (0.04 mol) and 7.84 g (0.04 mol) of α-bromo-*p*-toluenitrile in 60 mL toluene for 18 h to get 11 g (ca. 60%) of the salt; mp 326–329 °C (14). ^{1}H NMR ($CDCl_3$) (15) δ_H: 5.92 (2H, d, J = 15.6 Hz), 7.32 (2H, d, J = 8 Hz), 7.43 (2H, dd, J = 2.3, 8.2 Hz), 7.57–7.61 (6H, m), 7.73–7.83 (9H, m). ^{13}C NMR (DMSO) ($J_{P\text{-}C}$) δ_C: 29.17 (d, J = 46.6 Hz, P-CH_2), 112.22 (d, J = 3.8 Hz), 118.50 (d, J = 85.3 Hz, C-1 of P-Ph), 119.37 (d, J = 2 Hz), 131.26 (d, J = 12.5 Hz, C-3 of P-Ph), 132.80 (d, J = 5.4 Hz), 133.64 (d, J = 3 Hz, C-4 of P-Ph), 135.09 (d, J = 10 Hz, C-2 of P-Ph), 135.15 (d, J = 8.2 Hz), 136.32 (d, J = 2.7 Hz). ^{31}P NMR ($CDCl_3$) δ_P: 25.12. Anal. calcd. for $C_{26}H_{21}BrNP$ (%): C 68.12, H 4.58, N 3.06; found: C 68.10, H 4.63, N 3.17.

The target ylide **1** was prepared by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 1:2:1 ratio, as shown in procedure B. The yellow material that remained after evaporation of the solvent was triturated with diethyl ether to afford a solid material, which was recrystallized from acetonitrile to give 1.80 g of yellow crystals (ca. 45%); mp 276–278 °C. IR υ_{max} (cm^{-1}): 2216, 1594, 1285, 1263, 1177, 1141, 1101, 994, 695, 544, 514. ^{1}H NMR ($CDCl_3$) δ_H: 3.88 (2H, s), 6.95 (2H, d, J = 8 Hz), 7.09 (2H, d, J = 8 Hz), 7.16 (2H, d, J = 8 Hz), 7.25–7.28 (2H, m), 7.30–7.34 (1H, m), 7.40–7.45 (6H, m), 7.54–7.61 (9H, m). ^{13}C NMR ($CDCl_3$) ($J_{P\text{-}C}$) δ_C: 51.3 (d, J = 126 Hz, P=C), 62.9 (CH_2), 106.5 ($C{\equiv}N$), 120.13, 126.55 (d, J = 92 Hz, C-1 of P-Ph), 128.37, 128.77, 129.10 (d, J = 12 Hz, C-3 of P-Ph), 131.17 (2C), 131.46 (d, J = 9 Hz), 132.37 (d, J = 5.4 Hz), 132.67 (d, J = 3 Hz, C-4 of P-Ph), 132,46 (d, J = 9.7 Hz), 134.48 (d, J = 10 Hz, C-2 of P-Ph), 142.65 (d, J = 9.5 Hz). ^{31}P NMR ($CDCl_3$) δ_P: 19.36. MS m/z: 531 ($M^{+\cdot}$, 2), 440 (25), 392 (14), 376 (16), 277 (18), 262 (68), 183 (55), 105 (100). Anal. calcd. for $C_{33}H_{26}NO_2PS$ (%): C 74.58, H 4.90, N 2.64, S 6.03; found: C 74.71, H 5.12, N 3.01, S 5.68.

[(Benzylsulfonyl)(4-nitrophenyl)methylene](triphenyl)phosphorane (2)

Obtained by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 1:2:1 ratio. Yield: 72%, mp 275 to 276 °C (3). IR υ_{max} (cm^{-1}): 1582, 1490, 1334, 1284, 1264, 1142, 1107, 992, 936, 695 (3). ^{1}H NMR ($CDCl_3$) δ_H (3): 3.86 (2H, s), 6.84 (2H, d, J = 8.9 Hz), 7.11 (2H, d, J = 7.1 Hz), 7.29–7.34 (3H, m), 7.43–7.48 (6H, m), 7.56–7.66 (9H, m), 7.71 (2H, d, J = 8.8 Hz). ^{13}C NMR ($CDCl_3$) ($J_{P\text{-}C}$) δ_C: 54.03 (d, J = 124 Hz, P=C), 63.10, 123.10, 126.00 (d, J = 92 Hz, C-1 of P-Ph), 128.55, 128.87, 129.29 (d, J = 12 Hz, C-3 of P-Ph), 130.53 (d, J = 6 Hz), 131.00, 131.52, 132.93 (d, J = 3 Hz, C-4 of P-Ph), 134.63 (d, J = 10 Hz, C-2 of P-Ph), 143.11, 145.81 (d, J = 10 Hz). ^{31}P NMR ($CDCl_3$) δ_P: 19.21. MS m/z: 551 ($M^{+\cdot}$, 20), 460 (38), 412 (18), 396 (16), 277 (85), 262 (100), 201 (22), 183 (96), 108 (36), 91 (85). Anal. calcd. for $C_{32}H_{26}NO_4PS$ (%): C 69.69, H 4.74, N 2.54, S 5.81; found: C 69.49, H 4.80, N 2.70, S 5.28.

[(Benzylsulfonyl)(3-nitrophenyl)methylene](triphenyl)phosphorane (3)

The quaternary salt, 3-nitrobenzyltriphenylphosphonium chloride (**$Ph_3P^+CH_2$*m*-NO_2-$C_6H_4Cl^-$**), was prepared by refluxing 10.49 g (0.04 mol) of triphenylphosphine and 6.9 g (0.04 mol) of 3-nitrobenzyl chloride in 30 mL benzene for 28 h. After cooling, the solid was collected and washed with diethyl ether to obtain 11 g (~63%) of the salt; mp 255–258 °C (16). ^{1}H NMR ($CDCl_3$) δ_H: 6.08 (2H, d, J = 15.2 Hz), 7.29 (1H, t, J = 8 Hz), 7.58–7.64 (7H, m), 7.74–7.76 (3H, m), 7.84–7.89 (6H, m), 7.95 (1H, d, J = 8 Hz), 8.04 (1H, d, J = 8 Hz). ^{13}C NMR ($CDCl_3$) ($J_{P\text{-}C}$) δ_C: 30.18 (d, J = 46.8 Hz, P-CH_2), 118.01 (d, J = 85.4 Hz, C-1 of P-Ph), 123.41 (d, J = 3.4 Hz), 126.17 (d, J = 5 Hz), 130.31 (d, J = 3 Hz), 130.81 (d, J = 12.5 Hz, C-3 of P-Ph), 131.17 (d, J = 19.6 Hz), 134.98 (d, J = 10 Hz, C-2 of P-Ph), 135.65 (d, J = 3 Hz, C-4 of P-Ph), 139.41 (d, J = 5.4 Hz), 148.14 (d, J = 3.6 Hz). ^{31}P NMR ($CDCl_3$) δ_P: 25.55. MS m/z: 398 ($M^{+\cdot}$ – Cl^-). Anal. calcd. for $C_{25}H_{21}ClNO_2P$ (%): C 69.20, H 4.84, N 3.23; found: C 69.14, H 4.86, N 3.32.

The target ylide **3** was obtained by treating the salt with BuLi followed by the addition of phenylmethanesulfonyl fluoride in a 2:2:1 ratio, as per procedure A. The residual oil was triturated and recrystallized from ethyl acetate to give 2.68 g of yellow crystals (ca. 65%) of the target ylide: mp 233–235 °C. IR υ_{max} (cm^{-1}): 1518, 1438, 1340, 1276, 1257, 1100, 1012, 997, 745, 693, 551. ^{1}H NMR ($CDCl_3$) δ_H: 3.95 (2H, s), 7.13–7.17 (3H, m), 7.23–7.27 (3H, m), 7.40–7.44 (6H, m), 7.51–7.61 (10H, m), 7.63–7.65 (1H, m), 7.73–7.75 (1H, m). ^{13}C NMR ($CDCl_3$) ($J_{P\text{-}C}$) δ_C: 48.71 (d, J = 128 Hz, P=C), 62.7 (CH_2), 119.40 (d, J = 1 Hz), 126.47 (d, J = 92 Hz, C-1 of P-Ph), 127.87, 128.12, 128.33, 128.39 (d, J = 3.7 Hz), 128.69 (d, J = 12 Hz, C-3 of P-Ph), 130.79, 130.97, 132.16 (d, J = 3 Hz, C-4 of P-Ph), 133.97 (d, J = 10 Hz, C-2 of P-Ph), 137.81 (d, J = 10 Hz), 140.18 (d, J = 4.5 Hz), 147.20. ^{31}P NMR ($CDCl_3$) δ_P: 20.3. MS m/z: 551 ($M^{+\cdot}$, 2), 461 (12), 412 (8), 396 (10), 277 (60), 262 (100), 201 (15), 183 (84), 108 (38), 91 (96). Anal. calcd. for $C_{32}H_{26}NO_4PS$ (%): C 69.69, H 4.72, N 2.54, S 5.81; found: C 69.80, H 4.82, N 2.50, S 5.46.

[(Benzylsulfonyl)(4-chlorophenyl)methylene](triphenyl)phosphorane (4)

The quaternary salt, 4-chlorobenzyltriphenylphosphonium chloride (**$Ph_3P^+CH_2$*p*-Cl-$C_6H_4Cl^-$**), was prepared by refluxing 10.49 g triphenylphosphine (0.04 mol) and 6.5 g 4-chlorobenzyl chloride (0.04 mol) in 70 mL toluene for 21 h. After cooling, the solid was filtered and washed with diethyl ether to obtain 13.15 g (ca. 78%) of the salt: mp 290–293 °C (17, 18). ^{1}H NMR ($CDCl_3$) (15) δ_H: 5.71 (2H, d, J = 14.8 Hz), 7.0 (2H, d, J = 8 Hz), 7.11–7.12 (2H, m), 7.55–7.59 (6H m), 7.69–7.80 (9H, m). ^{13}C NMR ($CDCl_3$) ($J_{P\text{-}C}$) δ_C: 30.11 (d, J = 46.2 Hz, P-CH_2), 118.40 (d, J = 85 Hz, C-1 of P-Ph), 126.99 (d, J = 6.9 Hz), 129.26 (d, J = 3.2 Hz, C-4 of P-Ph), 130.61 (d, J = 12.5 Hz, C-3 of P-Ph), 133.69 (d, J = 5.4 Hz), 134.75 (d, J = 4.7 Hz), 135.06 (d, J = 10 Hz, C-2 of P-Ph), 135.38. ^{31}P NMR ($CDCl_3$) δ_P: 24.79. MS m/z: 389/387 ($M^{+\cdot}$ + 2/$M^{+\cdot}$ – Cl^-). Anal. calcd. for $C_{25}H_{21}Cl_2P$ (%): C 70.92, H 4.96; found: C 70.90, H 5.02.

The target ylide **4** was prepared by treating the salt with BuLi followed by phenylmethanesulfonyl fluoride in a 2:2:1

ratio, as shown in procedure A. The obtained colourless material was recrystallized from ethyl acetate to give 2.59 g (ca. 64%) of the ylide: mp 232–234 °C. IR υ_{max} (cm^{-1}): 1584, 1485, 1436, 1269, 1104, 1018, 935, 757, 732, 694, 542. ^{1}H NMR (CDCl$_3$) δ_H: 3.97 (2H, s), 6.98 (2H, d, J = 8 Hz), 7.05–7.15 (4H, m), 7.27–7.30 (2H, m), 7.35–7.39 (7H, m), 7.48–7.53 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) δ_C: 46.6 (d, J = 129 Hz, P=C), 62.06 (CH$_2$), 127.68 (d, J = 92 Hz, C-1 of P-Ph), 128.05 (2C), 128.17 (d, J = 1.4 Hz), 128.63, 128.68 (d, J = 1.9 Hz), 128.89 (d, J = 12 Hz, C-3 of P-Ph), 131.61, 131.69, 132.18 (d, J = 3 Hz, C-4 of P-Ph), 134.16 (d, J = 3.6 Hz), 134.28 (d, J = 10 Hz, C-2 of P-Ph), 136.63 (d, J = 4 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 19.61. MS *m/z*: 542/540 (M$^{+\cdot}$ + 2/M$^{+\cdot}$, 35/60%), 415 (30), 401 (45), 385 (80), 351 (40), 277 (100), 262 (75), 201 (45), 199 (42), 183 (80), 139 (58), 1 (64). Anal. calcd. for $C_{32}H_{26}ClO_2PS$ (%): C 71.04, H 4.81, S 5.92; found: C 71.21, H 4.92, S 6.03.

[(Benzylsulfonyl)(3-chlorophenyl)methylene](triphenyl)-phosphorane (5)

The quaternary salt, 3-chlorobenzyltriphenylphosphonium chloride (**$Ph_3P^+CH_2$*m*-Cl-$C_6H_4Cl^-$**), was prepared by refluxing 10.49 g of triphenylphosphine (0.04 mol) with 6.44 g of 3-chlorobenzyl chloride (0.04 mol) in benzene for 48 h to obtain 13.90 g (ca. 82%) of the salt: mp 320–323 °C (19). ^{1}H NMR (CDCl$_3$) δ_H: 5.66 (2H, d, J = 15.2 Hz), 6.87 (1H, d, J = 2 Hz), 7.02 (1H, t, J = 8 Hz), 7.12 (1H, d, J = 7.6 Hz), 7.15 (1H, d, J = 7.6 Hz), 7.57–7.61 (6H, m), 7.71–7.81 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) δ_C : 30.62 (d, J = 46.5 Hz, P-CH$_2$), 118.30 (d, J = 85.40 Hz, C-1 of P-Ph), 128.91 (d, J = 3.8 Hz), 130.35 (d, J = 8.4 Hz), 130.55 (d, J = 3.3 Hz, C-4 of P-Ph), 130.70 (d, J = 12.5 Hz, C-3 of P-Ph), 130.76, 131.73 (d, J = 5.3 Hz), 134.72 (d, J = 3.8 Hz), 134.98 (d, J = 10 Hz, C-2 of P-Ph), 135.51 (d, J = 2.7 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 25.05. MS *m/z*: 389/387 (M$^{+\cdot}$ + 2/M$^{+\cdot}$ – Cl$^-$). Anal. calcd. for $C_{25}H_{21}Cl_2P$ (%): C 70.92, H 4.96; found: C 70.96, H 4.96.

The target ylide **5** was prepared by treating the obtained salt with BuLi and phenylmethanesulfonyl fluoride according to procedure A, in a 2:2:1 ratio. The obtained colorless material was recrystallized from ethyl acetate to obtain 3.25 g of the pure colorless crystals (ca. 80%) of the target ylide mp 216–218 °C. IR υ_{max}(cm^{-1}): 1584, 1436, 1270, 1103, 811, 760, 542, 503. ^{1}H NMR (CDCl$_3$) δ_H: 3.99 (2H, s), 6.90–7.00 (2H, m), 7.04 (1H, s), 7.10–7.15 (2H, m), 7.25–7.31 (4H, m), 7.37–7.40 (6H, m), 7.48–7.55 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) δ_C: 47.5 (d, J = 129 Hz, P=C), 62.29 (CH$_2$), 125.6 (d, J = 2 Hz), 127.53 (d, J = 92 Hz, C-1 of P-Ph), 128.13, 128.64, 128.71, 128.89 (d, J = 12 Hz, C-3 of P-Ph), 128.98, 131.59 (d, J = 2.1 Hz), 132.06 (d, J = 2.9 Hz), 132.24 (d, J = 3 Hz, C-4 of P-Ph), 134.17, 134.30 (d, J = 10 Hz, C-2 of P-Ph), 134.89 (d, J = 4.1 Hz), 137.7 (d, J = 9 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 19.84. MS *m/z*: 542/540 (M$^{+\cdot}$ + 2/M$^{+\cdot}$, 8/18%), 451/449 ($^{37/35}$Cl – M$^+$ – PhCH$_2$, 35/100), 401 (50), 385 (85), 351 (40), 262 (46), 241 (40), 183 (85), 165 (78), 139 (75). Anal. calcd. for $C_{32}H_{26}ClO_2PS$ (%): C 71.04, H 4.81, S 5.92; found: C 71.17, H 4.96, S 5.66.

[(Benzylsulfonyl)(phenyl)methylene](triphenyl)phosphorane (6)

Obtained by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 2:2:1 ratio. Yield: 78%; mp 210–212 °C (1, 3). IR υ_{max} (cm^{-1}): 1590, 1484, 1435, 1266, 1240, 1094, 1021, 939, 708, 692, 545, 526. ^{1}H NMR (CDCl$_3$) (1) δ_H: 4.00 (2H, s), 7.03–7.15 (4H, m), 7.26–7.37 (12H, m), 7.47–7.54 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) (1) δ_C: 46.80 (d, J = 129 Hz, P=C), 61.83 (CH$_2$), 125.85 (d, J = 2 Hz), 127.91, 128.09 (d, J = 92 Hz, C-1 of P-Ph), 128.13, 128.50, 128.73 (d, J = 12 Hz, C-3 of P-Ph), 131.70, 131.94 (d, J = 3 Hz, C-4 of P-Ph), 134.27 (d, J = 10 Hz, C-2 of P-Ph), 135.20 (d, J = 9 Hz), 135.29 (d, J = 9 Hz), 135.94 (d, J = 4 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 19.61 (1). MS *m/z*: 506 (M$^{+\cdot}$, 60), 416 (57), 415 (48), 368 (64), 351 (90), 273 (18), 165 (64), 105 (100). Anal. calcd. for $C_{32}H_{27}O_2PS$ (%): C 75.89, H 5.34, S 6.32; found: C 75.85, H 5.44, S 6.21.

[(Benzylsulfonyl)(4-methylphenyl)methylene](triphenyl)-phosphorane (7)

Obtained by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 2:2:1 ratio. Yield: 74%; mp 186–189 °C (1). IR υ_{max} (cm^{-1}): 1625, 1502, 1483, 1435, 1264, 1244, 1144, 1106, 1094, 1043, 1028, 935, 864, 788, 754, 714, 694 (1). ^{1}H NMR (CDCl$_3$) (1) δ_H: 2.24 (3H, s), 3.99 (2H, s), 6.87 (2H, d, J = 8 Hz), 7.13–7.16 (4H, m), 7.24–7.36 (9H, m), 7.45–7.52 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) δ_C: 21.5 (CH$_3$), 46.6 (d, J = 129 Hz, P=C), 61.6 (CH$_2$), 128.30 (d, J = 92 Hz, C-1 of P-Ph), 128.58 (d, J = 12 Hz, C-3 of P-Ph), 128.63, 128.75, 128.97 (d, J = 1 Hz), 131.73, 131.86 (d, J = 3 Hz, C-4 of P-Ph), 131.96, 132.01, 134.26 (d, J = 10 Hz, C-2 of P-Ph), 135.63 (d, J = 2 Hz), 136.11 (d, J = 4 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 19.49. MS *m/z*: 520 (M$^{+\cdot}$, 60), 429 (50), 416 (5), 380.7 (40), 365 (100), 277 (5), 262 (30), 165 (65), 119 (90), 91 (75). Anal. calcd. for $C_{33}H_{29}O_2PS$ (%): C 76.15, H 5.58, S 6.15; found: C 76.17, H 5.64, S 5.79.

[(Benzylsulfonyl)(4-methoxyphenyl)methylene](triphenyl)-phosphorane (8)

Obtained by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 2:2:1 ratio. Yield: 86%; mp 193–195 °C (3). IR υ_{max} (cm^{-1}): 2829, 1598, 1503, 1438, 1242, 1095, 1049, 750, 694 (3). ^{1}H NMR (CDCl$_3$) (3) δ_H: 3.75 (3H, s), 4.13 (2H, s), 6.62 (2H, d, J = 8 Hz), 7.16–7.18 (4H, m), 7.27–7.29 (2H, m), 7.32–7.35 (7H, m), 7.45–7.50 (9H, m). ^{13}C NMR (CDCl$_3$) ($J_{P\text{-}C}$) δ_C: 45.85 (d, J = 129 Hz, P=C), 55.61 (CH$_3$), 61.55 (CH$_2$), 113.72, 126.97 (d, J = 8.4 Hz), 127.86, 128.28 (d, J = 92 Hz, C-1 of P-Ph), 128.60, 128.71 (d, J = 12 Hz, C-3 of P-Ph), 131.70, 131.87 (d, J = 3 Hz, C-4 of P-Ph), 132.04, 134.20 (d, J = 10 Hz, C-2 of P-Ph), 137.94 (d, J = 3 Hz), 158.35 (d, J = 2 Hz). ^{31}P NMR (CDCl$_3$) δ_P: 19.80. MS *m/z*: 536 (M$^{+\cdot}$, 40), 397.1 (25), 365 (30), 381 (100), 278 (50), 262 (55), 183 (70), 152 (40), 121 (50), 91 (75). Anal. calcd. for $C_{33}H_{29}O_3PS$ (%): C 73.88, H 5.41, S 5.97; found: C 73.80, H 5.51, S 5.55.

[(Benzylsulfonyl)(methyl)methylene](triphenyl)phosphorane (9)

Obtained by treating the obtained salt with BuLi followed by phenylmethanesulfonyl fluoride in a 2:2:1 ratio. Yield: 62%; mp 170–172 °C (1). ^{1}H NMR (CDCl$_3$) (1) δ_H: 1.58 (3H, d, J = 14 Hz), 3.97 (2H, s), 7.27 (5H, s), 7.7–7.4

Table 3. Conditions for kinetics and HPLC analysis of sulfonyl-stabilized phosphorus ylides **1**–**9** (**$Ph_3P{=}CGSO_2CH_2Ph$**).

Ylide	G	Internal standard	UV detector (λ, nm)	*T* range (K)	Eluent ($CH_3CN:H_2O$)
1	*p*-CNC_6H_4	1,2,4-Trichlorobenzene	256	495–533	60:40+0.1% AcOH
2	*p*-$NO_2C_6H_4$	Chlorobenzene	210	487–529	70:30
3	*m*-$NO_2C_6H_4$	Chlorobenzene	256	492–535	70:30
4	*p*-ClC_6H_4	Chlorobenzene	256	495–545	70:30
5	*m*-ClC_6H_4	Chlorobenzene	256	494–544	70:30
6	C_6H_5	1,3-Dichlorobenzene	210	501–545	62:38
7	*p*-$CH_3C_6H_4$	Chlorobenzene	256	479–524	60:40+0.1% AcOH
8	*p*-$CH_3OC_6H_4$	Chlorobenzene	256	475–520	60:40+0.1% AcOH
9	CH_3	1,2,4-Trichlorobenzene	210	470–512	60:40+0.1% AcOH

(15H, m). ^{31}P NMR ($CDCl_3$) (1) δ_P: 20.8. Anal. calcd. for $C_{27}H_{25}O_2PS$ (%): C 72.97, H 5.63, S 7.21; found: C 72.68, H 5.42, S 6.98.

Characterization of novel products of the pyrolysis of ylides 1–4

Ylide 1

trans-*4,4′-Dicyanostilbene (*p-*$NCC_6H_4CH{=}CHC_6H_4CN$-*p*)*

IR υ_{max} (cm^{-1}): 2224, 949, 773. ^{1}H NMR ($CDCl_3$) δ_H: 7.21 (2H, s), 7.63 (4H, d, *J* = 8 Hz), 7.69 (4H, d, *J* = 8 Hz). MS *m*/*z*: 231 (18), 230 ($M^{+\cdot}$, 100), 229 (44), 228 (13), 215 (15), 202 (12).

(4-Cyanobenzyl)benzyl sulfone ($4\text{-}NCC_6H_4CH_2SO_2CH_2C_6H_5$)

IR υ_{max} (cm^{-1}): 2229, 1731, 1664, 1496, 1313, 1120, 773, 644. ^{1}H NMR ($CDCl_3$) δ_H: 4.15 (2H, s), 4.24 (2H, s), 7.41–7.50 (7H, m), 7.70 (2H, d, *J* = 8 Hz). MS *m*/*z*: 271 ($M^{+\cdot}$, 13), 207 (40), 206 (34), 130 (11), 116 (49).

Ylide 2

(4-Nitrobenzyl)benzyl sulfone ($4\text{-}NO_2C_6H_4CH_2SO_2CH_2C_6H_5$)

IR υ_{max} (cm^{-1}): 1525, 1349, 1296, 1116, 907, 730. ^{1}H NMR ($CDCl_3$) δ_H: 4.20 (s, 2H), 4.26 (s, 2H), 7.44–7.48 (m, 5H), 7.55 (d, 2H, *J* = 8.8 Hz), 8.27 (d, 2H, *J* = 8.7 Hz).

Ylide 3

(3-Nitrobenzyl)benzyl sulfone ($3\text{-}NO_2C_6H_4CH_2SO_2CH_2C_6H_5$)

IR υ_{max} (cm^{-1}): 1528, 1352, 1320, 1256, 1118, 1077, 815, 699, 641. ^{1}H NMR($CDCl_3$) δ_H: 4.2 (2H, s), 4.28 (2H, s), 7.43–7.48 (5H, m), 7.61 (1H, t, *J* = 8 Hz), 7.76 (1H, d, *J* = 7.7 Hz), 8.18 (1H, brs), 8.28 (1H, dd, *J* = 1, 8.2 Hz). ^{13}C NMR ($CDCl_3$) + DEPT135 δ_C: 57.01 (CH_2), 59.81 (CH_2), 124.43, 126.33, 127.62, 129.4, 129.73, 129.89, 130.36, 131.09, 137.43, 145.5. MS *m*/*z*: 291 ($M^{+\cdot}$, 3), 227 (8), 178 (24), 165 (32), 152 (14), 105 (62).

Ylide 4

(4-Chlorobenzyl)benzyl sulfone ($4\text{-}ClC_6H_4CH_2SO_2CH_2C_6H_5$)

IR υ_{max} (cm^{-1}): 1492, 1300, 1116, 902, 724. ^{1}H NMR ($CDCl_3$) δ_H: 4.10 (2H, s), 4.18 (2H, s), 7.32 (2H, d, *J* = 8.4 Hz), 7.38–7.45 (7H, m). ^{13}C NMR ($CDCl_3$) + DEPT135 δ_C: 57.4 (CH_2), 58.8 (CH_2), 126.2, 127.8, 129.5, 129.6, 129.6, 131.2, 132.6, 135.8. MS *m*/*z*: 282 (2), 280 ($M^{+\cdot}$, 6), 279 (2), 219 (2), 218 (18), 217 (10), 216 (32), 127 (50), 126 (18), 125 (100), 91 (100).

Ylide 5

(3-Chlorobenzyl)benzyl sulfone ($3\text{-}ClC_6H_4CH_2SO_2CH_2C_6H_5$)

IR υ_{max} (cm^{-1}): 1598, 1476, 1318, 1118, 904, 728, 648, 609. ^{1}H NMR ($CDCl_3$) δ_H : 4.09 (2H, s), 4.19 (2H, s), 7.29 (1H, d, *J* = 8 Hz), 7.35 (2H, d, *J* = 8 Hz), 7.37–7.45 (6H, m). MS *m*/*z*: 283 (6), 281 ($M^{+\cdot}$ + 1, 18), 218 (18), 217 (14), 216 (30), 183 (8), 181 (22), 157 (15), 155 (10), 127 (24), 125 (50).

Kinetic measurements and product analysis

Stock solution (7 mL) was prepared by dissolving 6–10 mg of the ylide in acetonitrile as the solvent to give a concentration of 1000–2000 ppm. Internal standard was then added, the amount of which was adjusted to give the desired peak area ratio of ylide to standard (2.5:1). The solvent and the internal standard were selected because both are stable under the conditions of pyrolysis and they do not react with either ylide or product. The internal standards used in this study were chlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene. Each mixture was filtered before use to ensure a homogenous solution.

The weight ratio of the ylide with respect to the internal standard was calculated from the ratio of the ylide peak area to the peak area of the internal standard. The kinetic rate was obtained by tracing the rate of disappearance of the ylide with respect to the internal standard as follows:

An aliquot part (0.2 mL) of each solution containing the ylide and the internal standard was pipetted into the reaction tube, and the tube was placed in the pyrolyzer for 6 min under nonthermal conditions. A sample was analyzed using the HPLC probe with the UV detector at a wavelength of 256 or 210 nm, and the standardization value (A_o) was then calculated. Several HPLC measurements were obtained with an accuracy of ≥2%. The temperature of the pyrolysis block was then raised until approximately 10% pyrolysis was deemed to occur over 900 s. This process was repeated after each 10–15 °C rise in the temperature of the pyrolyzer until >90% pyrolysis was achieved. The relative ratios of the integration values of the sample and the internal standard (*A*) at the pyrolysis temperature were then calculated. At least three kinetic runs were carried out at each reaction temperature following each 10–15 °C rise in the pyrolyzer temperature to ensure reproducible values of *A*. Treatment of the kinetic data and calculation of Arrhenius parameters and reaction rate constants have been detailed elsewhere (10, 20, 21). The conditions for kinetic and HPLC analyses of the ylides **1–9** are summarized in Table 3.

Acknowledgements

One of the authors (R.F.A.) wishes to thank the College of Graduate Studies, Kuwait University for a PhD candidacy. Kuwait University Research Grant SC 01/99 and ANALAB and SAF Grant Nos. GS 01/01 and GS 03/01 are gratefully acknowledged.

References

1. R.A. Aitken, M.J. Drysdale, G. Ferguson, and A.J. Loug. J. Chem. Soc. Perkin Trans. 1, 875 (1998).
2. R.A. Aitken and M.J. Drysdale. J. Chem. Soc. Chem. Commun. 512 (1991).
3. B.A. Reith, J. Strating, and A.M. Van Leusen. J. Org. Chem. **39**, 2729 (1974).
4. A.M. Van Leusen, B.A. Reith, A.J.W. Iedema, and J. Strating. Recl. Trav. Chim. Pays–Bas, **91**, 37 (1972).
5. Y. Shen and J. Yao. J. Chem. Res. Synop. 394 (1996).
6. L. Engman. J. Org. Chem. **49**, 3559 (1984).
7. H. Güsten and M. Salzwedel. Tetrahedron, **23**, 187 (1967).
8. H. Ndayikengurukiye, S. Jacobs, and W. Tachelet. Tetrahedron, **53**, 13811 (1997).
9. Mass Spectrometry Data Centre. Eight peak index of mass spectra. 4th ed. Royal Society of Chemistry, Cambridge. 1991.
10. N.A. Al-Awadi, M.H. Elnagdi, K. Kaul, S. Ilingovan, and O.M.E. El-Dusouqui. J. Phys. Org. Chem. **12**, 1 (1999).
11. R. Taylor. *In* The chemistry of functional groups: Supplement B. *Edited by* S. Patai. John Wiley, Chichester. 1979. p. 876.
12. H.H. Dib, N.A. Al-Awadi, Y.A. Ibrahim, and O.M.E. El-Dusouqui. Tetrahedron, **59**, 9455 (2003).
13. R.A. Aitken, J.I.G. Cadogan, and I. Gosney. Phosphorus, sulfur and silicon. Vol. 101. OPA, Amsterdam. 1995. p. 281.
14. A. Mylona, J. Nikokavouras, and I.M. Takakis. J. Chem. Res. Miniprint, **12**, 3514 (1986).
15. C. Imrie, T.A. Modro, E.R. Rohwer, and C.C.P. Wagener. J. Org. Chem. **58**, 5643 (1993).
16. H.H. Mel’nikow, A.E. Kretow, and Z. Mel’zer. Zh. Obshch. Khim. **7**, 461 (1937).
17. H. Higashi. Bull. Chem. Soc. Jpn. **43**, 3236 (1970).
18. A. Shafiee, K.M. Semnani, and A. Foroumadi. J. Heterocycl. Chem. **33**, 671 (1996).
19. B.R. Baker and R.E. Gibson. J. Med. Chem. **14**, 315 (1971).
20. N.A. Al-Awadi, K. Kaul, and O.M.E. El-Dusouqui. J. Phys. Org. Chem. **13**, 499 (2000).
21. N.A. Al-Awadi, O.M.E. El-Dusouqui, K. Kaul, and H.H. Dib. Int. J. Chem. Kinet. **32**, 403 (2000).