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Gas Phase Thermolysis of Allylphosphines, Kinetic Study

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ABSTRACT

Diallylphenyl, allylbenzylphenyl and allylmethylphenyl phosphines were pyrolized in a stirred-flow reactor at 380–429°C/7-20 torr, using toluene as carrier gas. The reaction products were propene, 1-phospha-1,3-butadiene, 1-phospha-1,2-diphenylethylene and 1-phosphaethylene.

The phospha-alkenes formed evolve into cyclo addition products. The propene elimination reaction showed first-order kinetics with rate coefficients following the Arrhenius equations: Diallylphenylphosphine:

$$k(s^{-1}) = 10^{10.57 \pm 0.31} \exp(-143 \pm 4\ kJ/mol.RT)$$

Allylbenzylphenylphosphine:

$$k(s^{-1}) = 10^{9.71 \pm 0.47} \exp(-135 \pm 6\ kJ/mol.RT)$$

Allylmethylphenylphosphine:

$$k(s^{-1}) = 10^{9.61 \pm 0.61} \exp(-144 \pm 9\ kJ/mol.RT)$$

A six-center cyclic transition state unimolecular reaction mechanism, consistent with the above Arrhenius parameters, is proposed for the propene elimination reaction.

INTRODUCTION

The unimolecular elimination reaction in allylic systems represented by Scheme 1 has been extensively studied for x = oxygen [1], sulfur [2], and in less extent for nitrogen [3–6] and silicon [7–9] (R and R′ = alkyl, substituted alkyl or aryl group).

The allyl sulfides have the highest rate of pyrolysis, while the rate for the amines is somewhat higher or similar to that of the ethers [10]. Since the entropy of activation for this reaction has negative values, the 1–5 hydrogen shift should involve a six-center cyclic transition state. The kinetic deuterium isotope effect in the allyl ethers was found to be temperature dependent [1], a fact that, together with the lack of substituent effects on the reaction rate, was used as evidence to propose a non-planar transition state and a highly concerted mechanism.

The allyl sulfides, on the other hand, showed an important substituent effect on the rate of pyrolysis [2], while the kinetic deuterium isotope effect was practically temperature independent [11]. These facts suggested a polar transition state in which their higher reactivity was due to an enhanced acidic character of the α-H atom being transferred in a nonlinear 1–5 shift path. Through this reaction (scheme 1), it is possible to obtain products with the C=X moiety, such as thiocarbonyl compounds, for spectroscopic studies [12–17] or synthetic purposes.

In the present work, an attempt was made to extend the study of this reaction to the allylic phosphorus system. The possibility of obtaining

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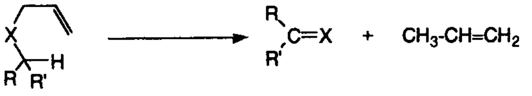


SCHEME 1

reactive phosphaalkenes through this reaction is interesting as a tool for synthetic phosphorus chemistry. Phosphaalkenes stabilized by bulky substituents have been obtained in solution [18]. Gas-phase formation of unstabilized phosphaalkenes has been achieved previously by flash vacuum pyrolysis *via* 1–2 elimination of HCl [19–22], and Me_3SiCl [23a] or H_2O [23b] or *via* 1–4 deshydrochlorination of γ-chloro vinylphosphines [24].

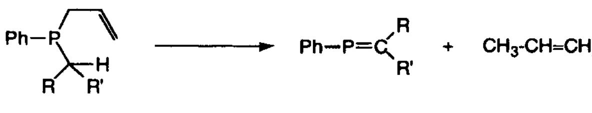
RESULTS AND DISCUSSION

Stoichiometry

Allyl phenyl phosphines **1a–c** (Scheme 2) were pyrolysed in a stirred flow system over the temperature range 378–430°C and total pressures between 7 and 21 torr, at conversions of up to 50%. Under these conditions, the reactants yielded as gas product a hydrocarbon mixture containing 98% propene, with minor amounts of C_2 and C_4 hydrocarbons. A nonvolatile fraction accumulated in the first cold trap, together with the unreacted phosphine.

With the diallylphenylphosphine **1a**, after cold distillation of the unreacted phosphine, the mass spectrum of the nonvolatile fraction showed the peak of m/e 296 and a fragmentation pattern which can be adscribed to the 1-phospha-1-phenyl-1,3-butadiene dimer [25, 26]. The analysis by ^{31}P NMR [25, 26] indicated that it consisted of a nearly 1 : 1 mixture of two isomers of 1,2-diphospha-1,2-diphenyl-3-ethenylcyclohex-5-ene **3a**, the product of a [4 + 2] cycloaddition reaction (Scheme 3), as is known for this kind of compound [27].

Addition of elemental sulfur to this mixture lead to the formation of two new systems in the same proportion, assigned to the corresponding dithiodiphosphacyclohexene isomers, **4a**, by assessment of the ^{31}P NMR data and mass spectra analysis [25, 26], and comparison with ^{31}P NMR data reported for similar compounds [27].

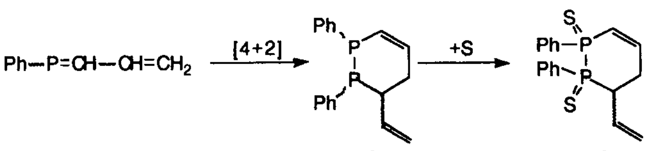


1 a-c

2 a-c

	a	b	c
R	H	H	H
R'	CH=CH2	Ph	H

SCHEME 2



2a

3a

4a

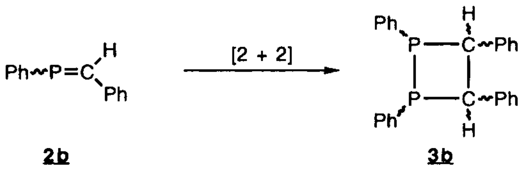
SCHEME 3

In the pyrolysis of the allylbenzylphenylphosphine **1b**, the mass spectroscopy analysis of the nonvolatile product fraction showed a peak of m/e 396 and a fragmentation pattern which can be attributed to the 1,2,3,4-tetraphenyl-1,2-diphosphetane **3b** [28] product of the head to head [2 + 2] cycloaddition of the 1,2-bisphenyl-1-phosphaethylene **2b**, produced during the pyrolysis (Scheme 4).

Its $^{31}P\{^1H\}$ NMR spectrum shows essentially two peaks at $\delta = -14.7$ and $\delta = -21.3$, which may correspond to this class of compound. In order to verify these results, we generated the phosphaethylene **2b** by the classical method of addition of a base (DBU) to an ethereal solution of benzylchlorophenylphosphine (Scheme 5).

The ^{31}P NMR spectrum of the product of this reaction shows the same two peaks at $\delta - 14.5$ and -21.6 in a 6:4 ratio. The 1,2-diphosphetane structure was confirmed by the ^{13}C NMR spectrum, which shows two doublets for two kinds of intracyclic carbon atoms ($\delta = 43.3$, $^1J_{PC} = 23.7$ Hz and $\delta = 42.87$, $^1J_{PC} = 25.7$ Hz) and two doublets for the quaternary carbon atoms of the two types of phenyl groups [28]. A 1,3-diphosphetane, product of a head to tail [2 + 2] cycloaddition reaction, would have shown instead a triplet for the intracyclic carbon (A_2B pattern). This suggests the presence of two isomers containing two phosphorus and two intracyclic carbon atoms respectively equivalent. The product **3b** may have five possible pairs of diastereoisomers (Scheme 6).

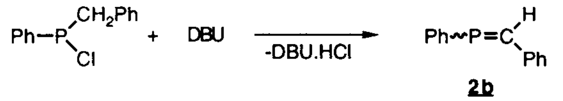
In the $\underline{C}$ and $\underline{E}$ diastereoisomers the phosphorus atoms are not magnetically equivalent and must show an AB system pattern in a ^{31}P NMR spectrum, then the two products obtained must be two of the other three ($\underline{A}$, $\underline{B}$, $\underline{D}$). We cannot explain why only two of them are formed and which of them is the most stable. All attempts to separate the two isomers were unsuccessful.



2b

3b

SCHEME 4

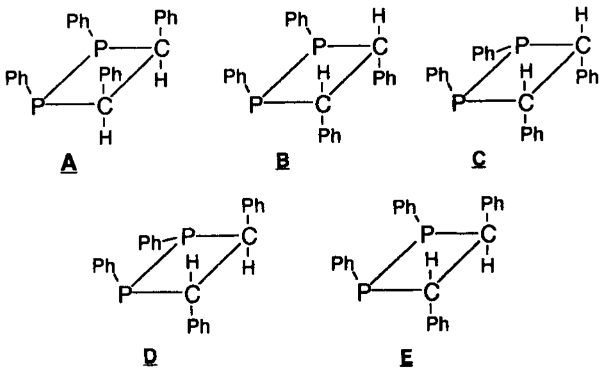


SCHEME 5

In the case of the pyrolysis of the allylmethylphenylphosphine **1c** [29] the analysis of the phosphorated products is more difficult than in the two previous examples, due to the high reactivity of the methylenephosphine **2c** formed. The ^{31}P NMR spectrum of the nonvolatile fraction shows the formation of products with resonance in the range of −10 to −50 ppm, typical of phosphorus (III) derivatives. These signals are certainly due to products of **2c** formed by intermolecular reactions leading to dimers, trimers, etc., as it is known for this compound [30]. In order to verify the formation of **2c**, the enophile 2,3-dimethylbutadiene was added to the carrier gas. The ^{31}P NMR spectrum of the nonvolatile products fraction showed, besides the signals of the above oligomers, a small peak at $\delta = -44.11$, a value very close to the reported 44.3 [30] for tetrahydrophosphinine. Under the present experimental conditions, it was not possible to direct the reaction selectively to the formation of the tetrahydrophosphinine.

KINETICS

The initial orders for the consumption of **1a** and **1b** for a three-fold increase of reactant inflow was 0.90 ± 0.06 and 1.0 ± 0.1, respectively, measured at 410 and 420°C and conversions of up to 40%. For **1c**, the order was 1.2 ± 0.2 at 458°C and 2.3 fold increase in reactant inflow, for conversions of about 15%. The order plots are shown in Figure 1. An order one was assumed for all the reactants. In Tables 1, 2 and 3 are collected the first order rate coefficients for **1a**, **1b** and **1c**, based on the propene rate of production, together with the experimental conditions for each run. For the calculation of these rate coefficients, it was assumed that the total reaction product outflow was twice that of propene, which implies that the phosphaalkene forms and leaves the reactor as a monomer in the same amount as propene. The linear least square fits of the rate coefficients yielded the Arrhenius parameters shown in Table 4. The error limits correspond to the standard error [31].



SCHEME 6

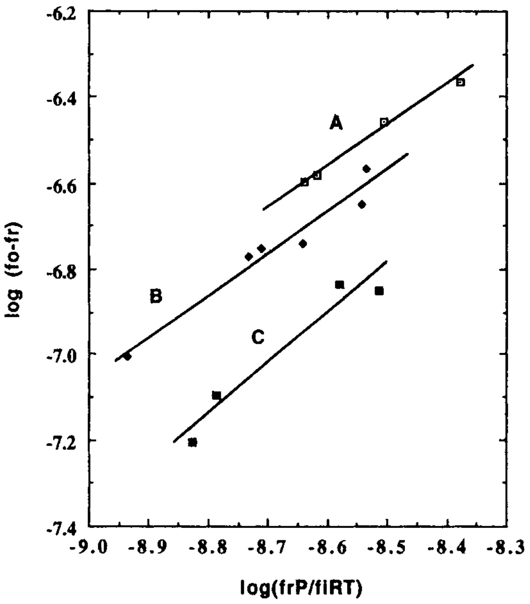


FIGURE 1 A: diallyl phenyl phosphine, B: allyl benzyl phenyl phosphine, C: allyl methyl phenyl phosphine, fo: reactant inflow, fr: reactant outflow, fi: total outflow, P: total pressure, T: absolute temperature, R: gas constant.

Table 4 shows the kinetic parameters for **1a**, **1b** and **1c** along with relevant data for homologous amine, ether, and sulfide systems. From the statistically corrected rate coefficients, calculated by using the respective Arrhenius equation, it can be inferred that **1a** and **1b** have about the same reactivity. They are about 8 times more reactive than **1c**. In regard to the relative reactivities of the S, P, N and O systems, it can be observed that allyl benzyl sulfide is about 6 times more reactive than **1b** and about 70 times more reactive than allyl benzyl ether. In the case of the methyl-X compounds, methyl allyl sulfide is 2, 37, and 18 times more reactive than the corresponding P, N and O homologue. The sequence S > P > N > O is then obtained, assuming that these pyrolyses proceed through similar mechanisms involving six center cyclic transition states. The more negative $\Delta S^{\neq}$ and Ea much lower than the homolytic C—P bond dissociation energy (about 285 ± 5 kJ.mol^{-1}) [32], together with their stoichiometries following scheme 1, support this assumption as pertaining to the phosphines. The activation parameters for the phosphines (Table 4) appear to be lower than those of the other systems. However, their A factors are just within the range of $10^{11.5\pm1.5}$ expected for six

TABLE 1 Stirred Flow Pyrolysis of Diallyl Phenyl Phosphine

T°C	(a) $k \times 10^4 s^{-1}$	(b) θ s	(c) %r (C_3H_6)	P torr	(d) $fr^0.10^8$	(e) fc / fr^0
378.5	1307	1.69	18.09	17.3	108.02	61
378.0	1215	1.73	17.39	14.3	87.36	61
391.5	2119	1.79	27.46	13.8	81.25	60
388.4	1927	1.71	24.84	15.6	83.02	69
400.5	3082	1.66	33.85	13.4	84.06	63
400.4	3004	1.63	32.91	18.4	80.75	87
401.2	2925	1.55	31.21	14.5	64.45	90
410.5	4591	1.66	43.31	11.1	75.19	54
410.5	4164	1.56	39.45	13.5	64.25	82
410.5	4102	1.53	38.60	14.2	67.56	84
411.0	4212	0.730	23.52	8.9	148.22	50
410.5	3875	0.678	20.80	10.4	207.50	45
421.0	6549	1.56	50.54	19.7	133.47	56
421.0	7145	0.802	36.44	8.3	153.27	40

(a) Rate coefficient. (b) Residence time. (c) Percent conversion based on propene measurement. (d) Reactant inflow, mol. s^{-1}. (e) Toluene to reactant flow ratio.

center cyclic transition states [33, 37]. Admittedly, the standard errors of the phosphines parameters make them the least accurate of the series, but they reflect experimental errors rather than other effects such as surface reactions or reactant consumption by a competitive radical chain reaction. An alternative mechanism for these pyrolyses involving allyl C—P bond homolysis as the initial step, generating free radicals, can reasonably be expected to yield a much more complex product mixture even if propene still results as the major component. Due to the higher temperature range needed for the pyrolysis of **1c**, this reactant suffers a small degree of fragmentation originating other minor products such as butene and hexadiene. The formation of the latter would imply the formation of radicals by P—C and C—C bond cleavages. This small deviation from stoichiometry (scheme 1), however, has no decisive influence in the estimation of the rate coefficients if only this stoichiom-

TABLE 2 Stirred Flow Pyrolysis of Allyl Benzyl Phenyl Phosphine

T°C	(a) $k \times 10^4 s^{-1}$	(b) θ s	(c) %r (C_3H_6)	P torr	(d) $fr^0.10^8$	(e) fc / fr^0
388.8	1055	1.67	14.95	12.8	49.97	98
388.7	1199	1.69	16.83	16.2	59.10	103
388.7	1083	1.69	15.48	13.7	50.87	101
388.8	1235	1.61	16.56	13.4	52.26	101
401.6	1374	1.65	18.51	13.3	53.29	94
399.2	1417	1.71	19.55	12.1	39.45	112
400.8	1703	1.65	22.00	15.6	62.81	101
400.3	1823	1.67	23.37	18.6	45.20	154
410.9	1940	1.69	24.70	14.1	42.12	126
411.5	1995	1.72	25.51	12.8	39.14	117
411.2	2131	1.56	25.00	15.5	61.05	99
410.7	2132	1.66	26.09	15.7	58.62	99
420.0	3098	0.943	23.81	6.9	41.55	110
419.2	3015	1.47	30.74	13.6	59.26	94
419.5	2936	1.60	31.98	17.0	69.81	92
421.0	3513	1.64	36.49	17.9	47.07	141
420.5	3303	0.881	22.53	10.0	78.82	117
421.2	3506	0.874	23.45	7.9	115.70	47
430.5	4767	0.884	29.36	7.8	71.05	75
429.5	4565	0.871	28.45	7.5	68.89	75
431.1	5169	0.852	30.57	8.0	55.92	100

Headings as in Table 1.

TABLE 3 Stirred Flow Pyrolysis of Allyl Methyl Phenyl Phosphine

T°C	(a) $k \times 10^4\ s^{-1}$	(b) θ s	(c) %r (C_3H_6)	P torr	(d) $fr^0.10^8$	(e) fc/fr^0
456.2	2399	0.706	14.49	10.7	101.6	76
458.0	1977	0.894	15.01	10.9	94.68	65
458.1	1782	0.929	14.21	8.95	43.71	112
458.0	2096	0.895	15.80	10.0	50.86	112
471.3	2576	0.946	19.59	8.36	53.73	82
467.5	2822	0.957	21.27	9.86	66.70	77
471.1	3360	0.901	23.24	10.7	65.98	90
471.2	3202	0.920	22.76	11.7	70.81	90
479.1	3675	1.55	36.29	13.2	46.07	91
481.8	3583	1.45	34.21	13.2	44.66	100
481.3	4639	1.55	41.79	15.0	46.01	103
481.4	3416	1.56	34.84	16.8	34.28	97
490.1	4914	0.945	31.72	10.8	56.71	98
490.5	5673	0.850	32.54	11.3	65.33	98
490.8	5430	0.854	31.68	10.2	55.77	104
490.9	5272	1.54	44.77	18.2	44.83	129
499.3	6922	0.883	37.93	11.8	56.90	113
499.7	7738	0.751	36.75	11.3	63.64	113
499.4	6387	0.798	33.76	11.4	42.02	156
499.4	8140	0.874	41.56	11.0	43.92	138

Headings as in Table 1.

etry is used to fix the **1c** extent of conversion. The difference in reactivity between **1a** or **1b** and **1c** suggests a substituent effect on the 1–5 H atom shift mechanism of these phosphines. This effect, although smaller than the one observed in the sulfide system, may indicate a polar character in their transition state, whereby a partial negative charge develops at the α-C atom, stabilized by the polarizability of the P atom, while a partial positive H atom is transferred to the allylic C atom, as previously proposed for the sulfides [2, 10]. In fact, the above reactivity sequence is similar to that of the polarizabilities of these atoms (S: 3.45, P: 4.42, N: 1.04, O: 0.73 $Å^3$) [34]. A substituent effect on the reaction rate would also imply the mechanism for the phosphines to be non-concerted as in the case of sulfides, with the C—P bond breaking as the rate determining step. This would explain the lower reactivity of the phosphines as compared with the sulfides, in which the C—S bond may be weaker than the C—P bond by about 20 $kJ \cdot mol^{-1}$.

EXPERIMENTAL

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-300 instrument. Mass spectra were obtained on a Kratos GLCMS RFA25 instrument.

Phenyldiallylphosphine **1a**. This was synthesized by a published method [25].

Allylbenzylphenylphosphine **1b**. A filtered solution of 0.08 mol of allylmagnesium bromide (obtained from 0.08 mol of allyl bromide and 0.16 mol of magnesium turnings in 100 ml of freshly distilled ether [35]) is added to a stirred solution of 0.07 mole of benzylphenylchlorophosphine in 200 ml of freshly distilled ether cooled at 0°C. When the addition is finished, the reaction mixture is stirred at room temperature for 1 hour, filtered and the solvent evaporated. **1b** is distilled at 10^{-3} torr in a 15 cm vigreux column at 98–100°C yielding 13.5 g (80%) of pure phosphine. $^{31}P\ \{^1H\}$ NMR (121.496 MHz, $CDCl_3$, H_3PO_4 ext.) $\delta = -22.5$. $^{13}C\ \{^1H\}$ NMR (75.469 MHz, $CDCl_3$, TMS ext.) $\delta = -31.8$ (d, $^1J_{PC} = 15.8$ Hz, $\underline{C}H_2$—Ph); $\delta = 34.5$ (d, $^1J_{PC} = 17.35$ Hz, $\underline{C}H_2CH$) $\delta = 116.8$ (d, $^3J_{PC} = 8.9$ Hz, $CH{=}\underline{C}H_2$) $\delta = 125.6$ (d, $^4J_{PC} = 2.3$ Hz, m-C) $\delta = 128$ (d, $^3J_{PC} = 6.7$ Hz, m'C) $\delta = 128.1$ (5, p'-C) δ 128.7 (s, p.C) $\delta = 129.4$ (d, $^3J_{PC} = 6.03$ Hz, o-C) $\delta = 132.3$ (d, $^2J_{PC} = 18.9$ Hz, o'-C) $\delta = 132.8$ (d, $^2J_{PC} = 6.8$ Hz, $\underline{C}H{=}CH_2$) $\delta = 137$ (d, $^1J_{PC} = 18.48$ Hz arom CP) $\delta = 137.4$ (d, $^2J_{PC}$ = arom $\underline{C}CH_2P$) (o, m, p benzyl group, o', m', p' phenyl group) ^1H NMR (300, 133 MHz, $CDCl_3$ TMS ext) $\delta = 2.54$ (d, $^2J_{PH} = 7.5$ Hz) 2H, $C\underline{H}_2$—CH=) $\delta = 3.1$ (bs, 2H, $C\underline{H}_2Ph$) $\delta = 4.99$ (m, 2H, $C\underline{H}_2{=}CH$) $\delta = 5.71$ (m, 1H, $C\underline{H}{=}CH_2$) $\delta = 7.07$–7.5 (m, 10H, Ph).

Allymethylphenylphosphine **1c**. A filtered solution of 0.1 mol of allylmagnesium bromide in 120 ml of ether is added dropwise to a stirred solution of 0.09 mol of chloromethylphenylphosphine in 150 ml of freshly distilled ether at 0°C. After the addition, the reaction mixture is stirred at room temperature for 1 hour, filtered and the solvent evaporated. **1c** is distilled as colorless liquid. b.p.35 torr: 124–126°C, 68% yield. $^{31}P\ \{^1H\}$ NMR (121.496 MHz,

TABLE 4 Kinetic Parameters for Allyl Compounds

Reactant	*log A*	*(a)* *Ea*	*(b)* $-\Delta S^{\neq}$	*(c)* k_{375}	*(c)* k_{400}	*(d)* *BDE*	*Ref.*
$CH_3{-}S{-}C{-}C{=}C$	11.23 ± 0.25	160 ± 3	41	0.75	2.2	265	2
$S(C{-}C{=}C)_2$	11.01 ± 0.06	138.2 ± 0.7	49	19	48		2
$PhCH_2{-}S{-}C{-}C{=}C$	10.93 ± 0.18	141 ± 2	50	19	49		2
$Ph{-}PCH_3(C{-}C{=}C)$	9.61 ± 0.61	144 ± 9	76	0.34	0.91	285	*
$Ph{-}P(C{-}C{=}C)_2$	10.57 ± 0.31	143 ± 4	57	2.8	7.5		*
$Ph{-}P(CH_2{-}Ph)(C{-}C{=}C)$	9.71 ± 0.47	135 ± 6	74	8.6	8.6		*
$CH_3NH(C{-}C{=}C)$	11.4	182	41	0.02	0.06	294	4
$H{-}N(C{-}C{=}C)_2$	11.04 ± 0.13	155 ± 1	48	0.96	2.8		4
$N(C{-}C{=}C)_3$	11.74 ± 0.07	160.1 ± 0.8	35	0.38	1.2		5
$c{-}C_6H_9{-}NH(C{-}C{=}C)$	11.44 ± 0.21	176 ± 2	41	0.18	0.61		6
$CH_3{-}O{-}C{-}C{=}C$	11.09 ± 0.02	174 ± 3	47	0.04	0.13	284	1
$O(C{-}C{=}C)_2$	11.91 ± 0.10	171.1 ± 0.1	37	0.33	1.1		1
$Ph{-}CH_2{-}O{-}C{-}C{=}C$	11.53 ± 0.03	172.4 ± 0.4	33	0.22	0.71		1

(a) Activation energy kJ · mol^{-1}. (b) Entropy of activation, J. $°K^{-1}$ mol^{-1} at 375°C. (c) Rate coefficient calculated at 375 and 400°C, s^{-1}, statistically corrected $\times 10^2$ (d) X-Allyl Bond Dissociation Energy (kJ mol^{-1}) estimated by group additivity method (ref. 37) and reported $\Delta°_{f298}$ for the radicals (ref. 38). The value for C—P is from ref. 32.

$CDCl_3$, H_3PO_4 ext.) $\delta = -39$ ppm. ^{13}C $\{^1H\}$ NMR (75.469 MHz, $CDCl_3$, TMS ext.) $\delta = 9.9$ (d, $^1J_{PC} = 15.4$ $\underline{Hz}$, $\underline{C}H_3$); $\delta = 35.4$ (d, $^1J_{PC} = 14.1$, $\underline{C}H_2CH{=}$) $\delta = 116.4$ (d, $^3J_{PC} = 8.1$ Hz, $\underline{C}H_2{=}CH$) $\delta = 128.9$ (d, $^3J_{PC} = 6.04$ Hz, m.C) $\delta = 128.14$ (s, p-C) $\delta = 131.17$ (d, $^2J_{PC} = 17.7$, o-C) $\delta = 132.8$ (d, $^2J_{PC} = 4.6$ Hz, $\underline{C}H{=}CH_2$) $\delta = 139.5$ (d, $^1J_{PC} = 15.6$ Hz, arom CP)^{1}H NMR (300, 133 MHz, $CDCl_3$ TMS ext) $\delta = 2.54$ (d, $^2J_{PH} = 3.5$ Hz, 3H, $C\underline{H}_3$) $\delta = 2.5$ (d, $^2J_{PH} = 7.5$, 2H, $C\underline{H}_2{-}CH{=}$) $\delta = 5.0$ (m, 2H, $C\underline{H}_2{=}CH$) $\delta = 5.7$ (m, ^{1}H, $C\underline{H}{=}CH_2$) $\delta = 7.32$–7.5 2 (m, 5H, arom).

The kinetics was carried out in a 265 mL quartz stirred-flow reactor [36], by injecting 10 mL of 0.04–0.05 molar solutions of the phosphines in dry deoxygenated toluene over periods of 20–30 minutes. Toluene was used as carrier gas because it is known to be a good hydrogen donor for inhibiting radical chain reactions. The reactants, solutions and reaction products were kept under argon. The experimental technique, reaction order measurement and rate coefficient calculation have been described elsewhere [10].

1a and **1b** were pyrolyzed in the stirred-flow system over the temperature range 378–430°C, total pressures between 7 and 21 torr, at conversions of up to 50% and residence times in the range 0.6–1.8 seconds.

1c was pyrolyzed over the temperature range 456–499°C under similar pressures, residence times and conversions between 14 and 41%. The gas hydrocarbon product mixture had the following average composition: C_2: 0.9 ± 0.6%, propene: 94 ± 2%,:$C_4$2.3 ± 0.9%,:$C_6$3 ± 1%.

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[26] Selected Data for **2a**, **3a** and **4a**. **2a**: $^{31}P\{^1H\}$ NMR. ($CDCl_3$): two isomers $\delta = 205.7$ and $\delta = 191.5$. **3a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P_1 = -64.2$, $\delta P_2 = -34.8$, $^1J_{PP} = 255.9$ Hz and $\delta P_1 = -21.4$, $\delta P_2 = 3.5$, $^1J_{PP} = 230.6$ Hz. Mass spectrum: m/e (%): 296 (25, M^+), 256 (75, M-PhPH), 148 (5, M/2), 108 (100, PhP). **4a**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta P_1 = 18.7$, $\delta P_2 = 32.17$, $^1J_{PP} = 52.2$ Hz and $\delta P_1 = 16.1$, $\delta P_2 = 31.8$, $^1J_{PP} = 53$ Hz. Mass spectrum: m/e (%): 360 (34, M^+), 328 (20, M-S), 296 (9, M-2S), 220 (40, M-PhPS), 188 (97, M-PhP-2S), 174 (28, M-2Ph-S).

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[28] Selected data for the mixture **3b**: $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta_1 = -14.7$ (60%), $\delta_2 = -21.3$ (40%). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 42.87$ (d, $^1J_{PC} = 25.7$ Hz, $\underline{C}HP$, 40%) $\delta = 43.3$ (d, $^1J_{PC} = 23.7$ Hz, $\underline{C}HP$, 60%) $\delta = 132.4$ (d, $^1J_{PC} = 17.6$ Hz, arom $\underline{C}P$, 40%) $\delta = 133.1$ (d, $^1J_{PC} = 13.7$ Hz, arom $\underline{C}P$, 60%) $\delta = 136.7$ (d, $^2J_{PC} = 7.7$ Hz, arom $\underline{C}CHP$, 40%) $\delta = 137.8$ (d, $^2J_{PC} = 9.5$ Hz, arom $\underline{C}CHP$, 60%) $\delta = 125-131$ and $\delta = 134-135.5$ signals corresponding to others aromatic carbons that can't be assigned. Mass spectrum m/e (%): 396 (8, M^+), 306 (2, M-PhCH) 216 (7, PhPPPh) 198 (66, M/2) 180 (38, PhCHCHPh).

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