Thermal Decomposition of Triphenylphosphonium Alkyl Ester Salts

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*In thermolyses of molten triphenylphosphonium alkyl ester bromides and chlorides, alkyl=methyl, ethyl, isopropyl, at 130 and 225°C, initial attack of the halide ion on the methyl group gives the methyl halide and ylid **1**, $Ph_3P=CH_2$, which can be methylated, or is protonated by the phosphonium salt with transylidation giving $Ph_3P^+\text{-}CH_3X^-$, X=Br, Cl. The initial reactions of the ethyl or isopropyl esters are with the halide ion, X^-, as a base giving ylid, **1**, which can be protonated by HX or by transylidation. The t-butyl ester generates $Ph_3P^+\text{-}CH_3X^-$ but no products of transylidation. The first-formed ylid **1**, can be trapped by reactive alkyl and acyl halides, and the transient ylidic esters decompose thermally to triphenyl phosphine oxide, $Ph_3P=O$, react further with unreacted phosphonium ester, or are trapped by added aldehyde in a Wittig reaction. The final product compositions are affected by a decrease in pressure, due to escape of volatile intermediates, and by replacement of the X^- halide ion by the less nucleophilic and basic tosylate ion. Reactions under reflux, in solution in chloroform, or in suspension in benzene, are similar to those of the molten salts, but yields are generally lower at the lower temperatures.*

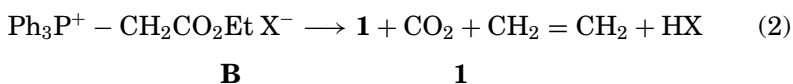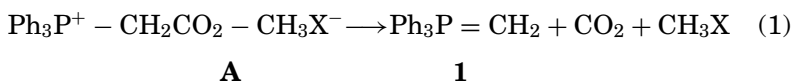**Keywords** Carboalkoxy phosphonium salts; thermolyses; solvent free

INTRODUCTION

Thermolyses of carboxylic and xanthate esters give the alkene through a spontaneous *syn* elimination.[1,2] The phosphonium salts, $R_3P^+\text{-}CH_2CO_2R'X^-$, decompose at temperatures between 130 and 225°C to give the alkene derived from R′.[3−5] The course of these and similar reactions is understandable in terms of mechanistic treatments of reactions in solution. The corresponding reactions of carboalkoxy phosphonium salts, shown as triphenyl derivatives, are complex, because the

initial ylidic products can react further or be trapped by added reagents, and these reactions control formation of the final products. In the two probable initial reactions of the molten phosphonium halide salts, the halide ions act as either nucleophiles or bases in the aprotic media, as expected in terms of the known chemistry of ylidic phosphonium salts[6] and general mechanistic concepts.

$$Ph_3P^+ - CH_2CO_2 - CH_3X^- \longrightarrow Ph_3P = CH_2 + CO_2 + CH_3X \quad (1)$$

$$\textbf{A} \qquad\qquad\qquad \textbf{1}$$

$$Ph_3P^+ - CH_2CO_2Et \; X^- \longrightarrow \textbf{1} + CO_2 + CH_2 = CH_2 + HX \quad (2)$$
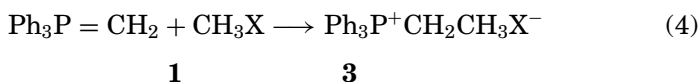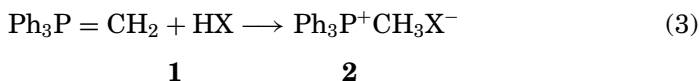
$$\textbf{B} \qquad\qquad\qquad \textbf{1}$$

We identify the phosphonium esters used in thermolysis alphabetically (A–F) and intermediates, products, and added reagents are identified by Arabic numerals.

The initially formed ylid **1** reacts rapidly with any electrophile, e.g., CH_3X, HX or unreacted phosphonium ion, and a variety of products are formed depending on the reaction conditions, for example, volatile species may be removed under reduced pressure, or ylid **1** may be trapped by an added electrophile.
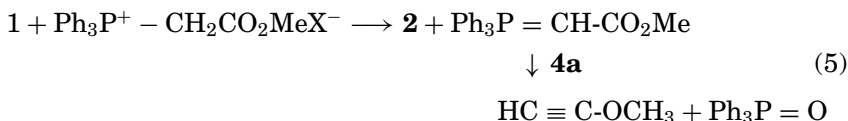
Reactions were generally carried out at temperatures slightly above the melting points of the salts, and thermolyses are them initially of the solid phosphonium salt, which soon melts and initial products decrease the melting point. The phosphonium salts have sharp melting points, with no indication of rapid decomposition, but they gradually decompose on heating in bulk. There is, therefore, some initial reaction of the crystalline salt, but reaction is largely in the melt, which is a viscous ionic liquid, and should accomodate the charge transfers occurring in the course of decomposition. There is uncertainty in the conditions of the overall reaction, which change during the decomposition. The high viscosity of the molten salt means that initially formed species will not diffuse apart rapidly, for example, adjacent cationic phosphonium esters, e.g., **A** or **B**, should react effectively with initially formed ylid in competition with added trapping agents. We used methyl, ethyl, isopropyl, and t-butyl derivatives in view of extensive mechanistic work on the effects of α-substituents on elimination and nucleophilic substitution. We performed a few experiments with an allylic ester group, and with introduction of a phenyl group, and we show that these structural modifications do not significantly affect the course of reaction.

The reaction can be carried out at atmospheric or reduced pressure, which affects secondary reactions of volatile species. The halogen acids formed in initial reactions of some substrates should not be strong acids in the molten salts and will probably exist largely as ion pairs or clusters; but, halide ions should be strong bases and nucleophiles towards compounds with which they can react readily in the melt.

The first formed ylid can be rapidly protonated or methylated giving phosphonium ions:

$$Ph_3P = CH_2 + HX \longrightarrow Ph_3P^+CH_3X^- \qquad (3)$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$Ph_3P = CH_2 + CH_3X \longrightarrow Ph_3P^+CH_2CH_3X^- \qquad (4)$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{3}$$

Alternatively, ylid **1** can react with its precursor, the cationic phosphonium ester, by transylidation,[6] generating a new ylid, e.g.

$$1 + Ph_3P^+ - CH_2CO_2MeX^- \longrightarrow \mathbf{2} + Ph_3P = CH\text{-}CO_2Me$$

$$\downarrow \mathbf{4a} \qquad (5)$$

$$HC \equiv C\text{-}OCH_3 + Ph_3P = O$$

Ylidic esters formed in this and similar reactions decompose thermally giving the triphenyl phosphine oxide, which is thermally stable and is a major product in these reactions. Except in special cases, ylides are not final products.

Formation of most of the thermolysis products can be explained in terms of the above reactions, plus those with added electrophiles, e.g., acyl and alkyl halides, and activated aldehydes in a Wittig reaction. In some conditions, an ylidic ester may react with a phosphonium ion with transylidation rather than by thermal decomposition, as in the reverse of the first step in Eq. (5). In the viscous ionic liquid, these reactions of intermediates may behave as if they are intramolecular and compete against the intermolecular trapping of the ylidic intermediates by added electrophiles, which give stable products.

The phosphonium ylides are labile compounds and the final products of their reactions depend on the physical conditions, including the removal of volatile intermediates under reduced pressure. The reactions that take place in the ionic liquids can also occur to some extent in inert organic liquids, although at lower temperatures and generally with lower yields than in the thermolyses. In these conditions, solubilities of the phosphonium esters play a key role, for example, the salts are soluble in chloroform, but not in benzene, where they react in

suspensions. In addition, escape of volatile intermediates should be slower at the relatively low temperatures in solvents than in molten salts.

These thermolysis are reactions, which can be carried out efficiently without a solvent, which is currently highly desirable.[7] The work is not directed to synthesis of particular products but has the potential to show how relatively small changes in reaction conditions of temperature or pressure, for example, can generate significant changes in product compositions. Organophosphorus compounds, particularly phosphonium salts and ylides, are essential building blocks in organic synthesis which makes understanding of their reactions practically important.[8]

RESULTS AND DISCUSSION

Various operating conditions were used, the temperature was varied but was generally above the melting point of the phosphonium salt, which decreased in the course of the reaction. Initial conditions are in Tables I–IV, but, as noted, they change during reaction and it is therefore difficult to treat medium effects on the products quantitatively. Probable courses of reaction are shown in Schemes 1 and 2 and final products of reaction in various conditions are shown in Tables I–IV.
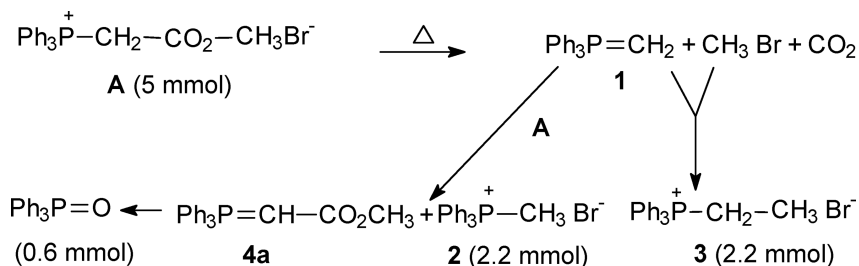
Most experiments were made with the bromide salts, but the chlorides and tosylates (p-toluenesulfonates) were also examined and anion effects are considered separately.

Decarboxylation in the course of reaction was confirmed by formation of $BaCO_3$, precipitation of silver halide confirmed formation and escape of a halogen acid or an alkyl halide, and decolorization of Br_2 confirmed formation of volatile alkenes or acetylenes.

TABLE I Thermolysis of Phosphonium Methyl Ester Salt A[a]

Ph_3P^+-CH_2-CO_2CH_3 X^- $\xrightarrow{\Delta}$	Ph_3P^+-CH_3X^-+	Ph_3P^+-CH_2-CH_3X^-	+ Ph_3PO
A	**2**[9]	**3**[9]	
a) $X^- = Br^-$ (5 mmol) $\xrightarrow[1.5\ h]{1At,\ 160°C}$	44%	44%	12%
b) $X^- = Br^-$ (4.8 mmol) $\xrightarrow[35\ min.]{1At,\ 140°C}$	48%	28%	24%
c) $X^- = Br^-$ (7.2 mmol) $\xrightarrow[163°C,\ 1h]{10mm\ Hg}$	16%	39%	
d) $X^- = Br^-$ (4.8 mmol) $\xrightarrow[134°C,\ 1\ h]{10\ mm\ Hg}$	52%	8%	40%
e) $X^- = Cl^-$ (4 mmol) $\xrightarrow[1.3h]{1At.,\ 150°C}$	50%	---	50%

[a]CO_2 formation is omitted for clarity.

$$Ph_3\overset{+}{P}-CH_2-CO_2-CH_3 Br^- \quad \overset{\Delta}{\longrightarrow} \quad Ph_3P=CH_2 + CH_3 Br + CO_2$$

A (5 mmol)   **1**

A

$$Ph_3P=O \leftarrow Ph_3P=CH-CO_2CH_3 + Ph_3\overset{+}{P}-CH_3 Br^- \qquad Ph_3\overset{+}{P}-CH_2-CH_3 Br^-$$

(0.6 mmol)   **4a**   **2** (2.2 mmol)   **3** (2.2 mmol)

SCHEME 1 Reaction conditions: 160°C, 1 At., 1.5 h.

Reaction of the Phosphonium Methyl Ester Salts A

We assume that the initial reaction involves nucleophilic substitution by halide ion with fragmentation, Eq. (1), but the initially formed ylid can be methylated, Eq. (4), or react by transylidation, Eq. (5), generating methyltriphenylphosphonium halide **2**[9] and the new ylidic ester **4**, which spontaneously decomposes giving triphenyl phosphine oxide. Scheme 1 and Table I show products, and the course of thermolysis of the phosphonium methyl ester salt **A** under different conditions.

TABLE II Thermolysis of Phosphonium Ethyl Ester Salt B[a]

$Ph_3P^+-CH_2-CO_2CH_2CH_3X^-$ $\overset{\Delta}{\longrightarrow}$	$Ph_3P^+-CH_3X^-$ +	$\overset{Et}{\underset{O}{\overset{O}{\underset{}{}}}}$	+ Ph_3PO
B	**2**	**5a**	
a) X = Br⁻ (7 mmol)	73%	—	27%[b]
b) X⁻ = Br⁻ (4.7 mmol)	52%	—	48%
c) X = Br⁻ (7 mmol)[e]	55%	16%	27%
d) X⁻ = Br⁻ (4.7 mmol)	43%	—	58%
e) X = Cl⁻ (5.2 mmol)	95%	—	5%
f) X = TsO⁻ (5.8 mmol)[d]	12%	—	—
g) X = TsO⁻ (3.8 mmol)[e]	90%	—	10%

Conditions (arrows): a) 1 At, 152°C, 2h; b) 1 At, 160°C, 1.5 h; c) 10 mm Hg, 135°, 2.2h; d) 10 mm Hg, 160°, 1.5 h; e) 1At, 145°C, 2.3h; f) 20 mm Hg, 165°C, 1h; g) 1At, 142°C, 1h., LiBr

[a]Formation of $CH_2 = CH_2$, CO_2 and detection of unreacted starting material are omitted for clarity. [b]Ph_3PO was isolated and identified by Ir spectroscopy. [c]Unreacted starting material, SM, (2%) was detected by ^{1}H NMR spectroscopy. [d]SM (88%) was detected by ^{1}H NMR spectroscopy in the crude product. [e]Lithium p-toluenesulfonate in the crude product was detected by ^{1}H NMR spectroscopy.

TABLE III Thermolysis of Phosphonium Isopropyl Ester Salt C[a]

Ph₃P⁺-CH₂-CO₂-CH(CH₃)CH₃ Br⁻	$\xrightarrow[\text{1h}]{\Delta}$	$Ph_3P^+\text{-}CH_3Br^- +$	i-PrO C=O / Ph₃P=C / O=C CH₂-P⁺PH₃ X	$+ Ph_3PO$
C		**2**	**5b** [b]	
a) **C** (4.5 mmol)[c]	$\xrightarrow[\text{153°C}]{\text{1 At}}$	70%	4%	22%
b) **C** (4.5 mmol)[d]	$\xrightarrow[\text{152°C}]{\text{10 mm Hg}}$	40%	4%	35%

[a]Formation of CO_2, propene and the presence of non reactive starting material (SM) is omitted for clarity. [b]Conformation of **5b** is not known, but we assume that it is the same as that of **5a**. [c]SM (4%) was detected in the crude after reaction. [d]SM (21%) was detected after thermolysis.

Methylation of the reactive ylid **1** by the first-formed CH_3Br gives ethyl triphenylphosphonium bromide **3** [Eq. (4), whose ^{1}H-NMR spectrum is identical to that of a standard sample.[9] In general ethyltriphenylphosphonium halide **3** is a significant product, except for experiments c and d (Table I) where at reduced pressure CH_3Br is removed from the molten medium with less trapping of the initially formed ylid. Examples of these reactions are shown in Scheme 1 for thermolysis at 160°C for 1.5 h, at atmospheric pressure where phosphonium salts **2**, **3**, and $Ph_3P=O$ were identified by ^{1}H NMR spectroscopy.

Reactions of the Phosphonium Ethyl Ester Salts B

The initial reaction of the ethyl ester of the phosphonium halide, **B**, is apparently attack of halide ion, with elimination and fragmentation giving ethylene and CO_2. This reaction probably involves the halide ion as an effective base in the aprotic medium. The halogen acid readily protonates the reactive ylide **1**, but apparently not ethylene, because we

TABLE IV Thermolysis of Phosphonium t-Butyl Ester Salt D

$Ph_3P^+\text{—}CH_2\text{—}CO_2\text{—}CMe_3X^-$	$\xrightarrow[\text{1At}]{\Delta}$	$Ph_3P^+\text{—}CH_3X^- +$	SM[a]
D		**2**	**D**
a) $X^- = Br^-$ (4.4. mmol)	$\xrightarrow[\text{2.5 h}]{\text{210°C}}$	100%	—
b) $X^- = Cl^-$ (4.8 mmol)	$\xrightarrow[\text{2.3 h}]{\text{165°C}}$	95%	5%

Formation of isobulylene and CO_2 is omitted for clarity.

saw no products derived from an ethyl halide. A possible intramolecular reaction involves cyclic proton transfer to the ylidic methylene group, which would give the methyl phosphonium salt **2** as the only isolatable product. It would require the ester to take up the unfavorable E conformation,[10] and this reaction is apparently unimportant.

$$Ph_3\overset{+}{P}-CH_2-C=O \longrightarrow Ph_3\overset{+}{P} - CH_3\ X^- + CO_2 + CH_2 = CH_2$$

(structure **B** at left with H, $X^-\ CH_2$, CH_2, O; product labeled **2**)

(6)
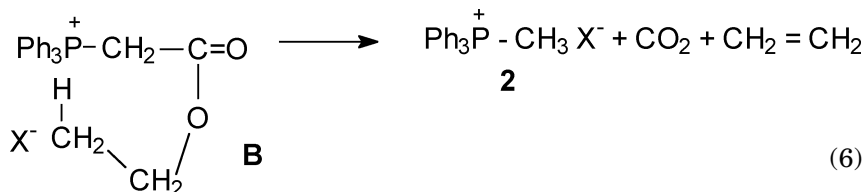
The subsequent overall reactions of the ethyl ester are similar to those observed with the methyl ester. The ylidic ethyl ester **4b**, is formed by transylidation and may decompose to the phosphine oxide or react with starting material giving ylidic ester **5a**.

$$Ph_3\overset{+}{P}\text{-}CH_2\text{-}CO_2\ C_2H_5\ X^-$$

B

+

$$Ph_3P=CH\text{-}CO_2C_2H_5$$

4b

$\longrightarrow$

(structure **5a**: H_5C_2-O, $C=O$, $Ph_3P=C$, $O=C-CH_2-\overset{+}{P}Ph_3$, X^-) + $C_2\ H_5\ OH$
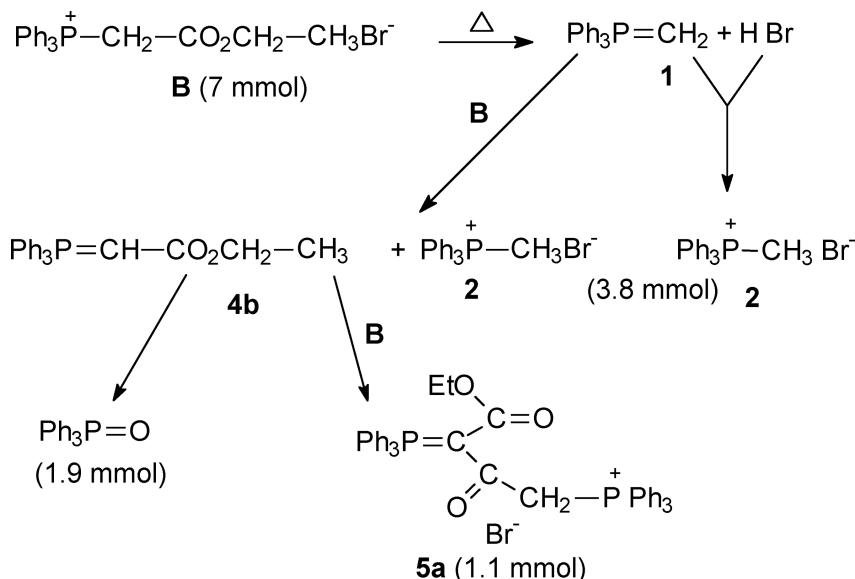
5a

(7)
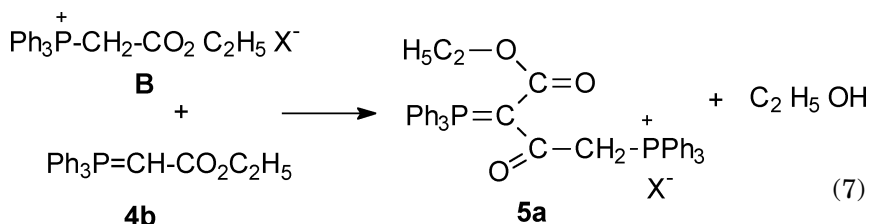
This ylid, **5a**, does not decompose during thermolysis, possibly because its high melting point, 183°C (bromide), allows it to separate out as a solid and be protected from further reactions. Compound **5a** had been prepared by reaction between the parent phosphonium salt, **B**, and the ylidic ester, **4b**, Eq. (7),[11] and its crystal structure was determined.[12]

Scheme 2 and Table II show the thermolysis of the phosphonium ethyl ester salt, **B,** with bromide, chloride or p-toluenesulfonate (tosylate) ion. The reaction is carried out at various pressures and temperatures. A main product is always the methyltriphenylphosphonium halide or tosylate, **2**, and in only one experiment (c) was the ylid- phosphonium salt **5a**, identified.

Under low pressure, HBr can escape from the molten reaction medium limiting protonation of initially formed ylid **1** and favoring formation of $Ph_3P=CH\text{-}CO_2Et$ (**4b**) by transylidation of reactive ylid **1** with phosphonium salt **B,** and the subsequent formation of the ylid-phosphonium salt **5a** [eq. (7) and Scheme 2].

Examples of these reactions are shown in Scheme 2 for thermolysis at 135°C for 2.2 hr and 10 mm pressure, and 2 mole% residual starting

$$Ph_3\overset{+}{P}-CH_2-CO_2CH_2-CH_3 Br^- \quad \xrightarrow{\Delta} \quad Ph_3P=CH_2 + H Br$$

B (7 mmol)   **1**

B

$$Ph_3P=CH-CO_2CH_2-CH_3 \quad + \quad Ph_3\overset{+}{P}-CH_3 Br^- \qquad Ph_3\overset{+}{P}-CH_3 \; Br^-$$

4b   **2**   (3.8 mmol)   **2**

B

$$Ph_3P=O$$
(1.9 mmol)

$$Ph_3P=C\overset{\displaystyle EtO\diagdown}{\underset{\displaystyle \diagup}{}}\begin{matrix}C=O\\ C\\ O\end{matrix}$$

EtO
      C=O
$Ph_3P=C$
      C
  O⫫ $CH_2-\overset{+}{P} Ph_3$
      Br^-

5a (1.1 mmol)

SCHEME 2 Thermolysis conditions are 135°C, 2.2 h, and 10 mm Hg.

material. Trapping of **1** by benzoyl chloride and benzyl bromide is shown later. Formation of ethylene and CO_2 are omitted for clarity.

Thermolysis of the tosylate salt of the ethyl ester phosphonium salt, **B**, gives only a low yield of $Ph_3P^+\text{-}CH_3^-OTos$ and no other identifiable product, probably because even in an ion pair tosylate ion is an ineffective base. However, lithium tosylate and equimolar bromide salt of the ethyl ester give a high yield of $Ph_3P^+\text{-}CH_3 \; Br^-$ because of the higher basicity of Br^- as compared with that of ^-OTos in the reaction medium.

Reactions of the Phosphonium Isopropyl Ester Salt C

The reactions outlined for thermolysis of the ethyl ester **B** control the decomposition of the isopropyl ester **C**, although there are minor differences in product ratios.

Table III shows the products of pyrolysis of the phosphonium isopropyl ester bromide **C**. At atmospheric and reduced pressure ^{1}H NMR spectroscopy indicates formation of the phosphonium ylide bromide **5b** as a minor product, from addition of the nucleophilic isopropylester ylid **4c** to the electrophilic carbonyl group of isopropyl ester phosphonium bromide **C**. As is general methyl triphenyl phosphonium bromide, **2**, is a major product in reactions of the bromide salt.

Reactions of the Phosphonium t-Butyl Ester Salt D

Decomposition of the t-butyl ester **D** is very simple in that there is no indication of formation of ylidic compounds as final products, and only the phosphonium salt **2** and unreacted **D** were identified (Table IV). Volatile materials were passed into Br_2-CCl_4, which was partially decolorized and removal of the solvent left a residue which had CH_3 and CH_2 ^{1}H NMR signals and is probably polymeric.

We saw no evidence for transylidation with $Ph_3P=CH_2$, which is consistent with an intramolecular concerted reaction was considered for decomposition of the ethyl ester **B**, Eq. (6). However, $Ph_3P=CH_2$, **1**, is trapped by added Ph-COCl, indicating that the reaction cannot be wholly intramolecular. The intermolecular reaction probably involves the halide ion as a base, and steric hindrance by the bulky t-butyl group should preclude transylidation. We note that addition of Ph-COCl may affect the composition of the reaction region, and therefore, the course of the reaction.

Structural Modifications

Reactions of the phosphonium benzyl ester salt, **E**, are similar to those of the methyl ester salts **A**, except that products are insensitive to pressure, probably because of the low volatility of the intermediate benzyl bromide which effectively traps $Ph_3P=CH_2$, **1**, Table V, to form Ph_3P^+-CH_2-CH_2-$PhBr^-$, **8**, detected by ^{1}H NMR spectroscopy in the crude product.

In a separate experiment the intermediate ylidic ester **4** was trapped by 4-nitrobenzaldehyde in a Wittig reaction, Eq. (9). Reaction of **E** in $CHCl_3$, under reflux, gave no product of trapping of $Ph_3P=CH_2$ by benzyl bromide generated in situ, whose concentration is probably too low for it to compete with transylidation, and subsequent formation of triphenyl phosphine oxide by decomposition of the ylidic ester (Table VI).

Thermolysis of the allylic ester, **F**, involves attack of Br^- giving the allyl bromide, **6**, bp. 70°C, which was isolated by distillation. Although

TABLE V Thermolysis of Phosphonium Benzyl Ester Salt E

Ph_3P^+-CH_2-CO_2CH_2-Ph Br^-	$\xrightarrow[\text{1 At, 1.5 h}]{115°C}$	Ph_3P^+-CH_3Br^- +	Ph_3P^+-CH_2-CH_2-Ph Br^-	+ $Ph_3P=O$
E (4.1 mmol)		**2**	**8**	
		43%	28%	29%
E (4.1 mmol)	$\xrightarrow[\text{9 mm Hg, 2 h}]{113°C}$	42%	27%	31%

TABLE VI Thermolyses of Phosphonium Alkyl Ester Salts in organic liquids[a]

$Ph_3P^+\text{-}CH_2\text{-}CO_2CH_3Br^-$		$Ph_3P^+\text{-}CH_3Br^-$	$+ Ph_3P^+\text{-}CH_2\text{-}CH_3Br^-$	$+ Ph_3P=O$
	$\xrightarrow[\text{61°C, 14 h}]{\text{CHCl}_3}$			
A (7.2 mmol)[b]		**2**[9]	**3**[9]	
		29%	10 %	13.7 %
$Ph_3P^+\text{-}CH_2\text{-}CO_2\text{-}CH_2\text{-}CH_3Cl^-$	$\xrightarrow[\text{80°C, 36 h}]{\text{Ph-H}}$	$Ph_3P^+\text{-}CH_3Cl^-$		
B (2.6 mmol)[c]		**2**		
		100%		
$Ph_3P^+\text{-}CH_2\text{-}CO_2\text{-}C(CH_3)_3Br^-$	$\xrightarrow[\text{80°C, 20 h}]{\text{Ph-H}}$	$Ph_3P^+\text{-}CH_3Br^-$	+ SM	
D (1.8 mmol)[d]		**2**		
		10 %	90%	
$Ph_3P^+\text{-}CH_2\text{-}CO_2CH_2PhBr^-$	$\xrightarrow[\text{61°C, 8 h}]{\text{CHCl}_3}$	$Ph_3P^+\text{-}CH_3Br^-$	+ SM +	$Ph_3P=O$
E (4.1 mmol)[e]		**2**	**E**	
		17%	69%	14%

[a]Alkenes and CO_2 are omitted for clarity. [b]Thermolysis is carried out in solution; SM: starting material (47%) was detected. [c]Methyl phosphonium chloride **2** was identified by Ir spectroscopy and comparison with a standard for reaction in benzene suspension . [d]Benzene suspension . [e]Reaction in CHCl$_3$ solution with no formation of $Ph_3P^+\text{-}CH_2\text{-}CH_2\text{-}Ph\ Br^-$.

allyl bromide is a reactive electrophile it did not react with $Ph_3P=CH_2$ and $Ph_3P^+\text{-}CH_3Br^-$, **2**, formed by transylidation, was a final product, eq. (8). This system was not examined in detail.

$$Ph_3P^+\text{-}CH_2-CO_2-CH_2-CH=CH_2Br^- \xrightarrow[\text{1 At., 1.5 h}]{130°C} Ph_3P=CH_2 + CH_2=CH-CH_2Br + CO_2$$

<div align="center">

F   **1**

</div>

$$Ph_3P=O \longleftarrow Ph_3P=CH-CO_2-CH_2-CH=CH_2 + Ph_3P^+\text{-}CH_3Br^-$$

<div align="center">

2

</div>

$$(8)$$
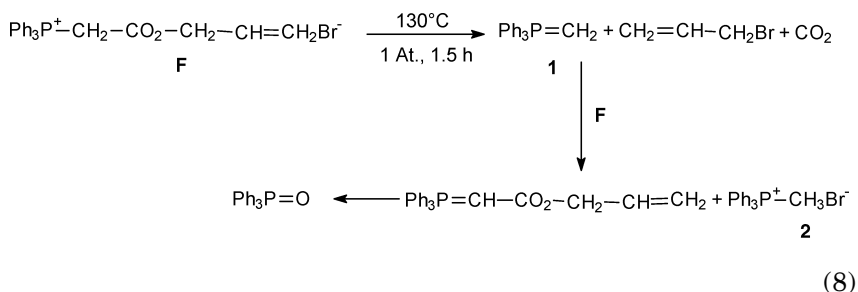
Decompositions in Organic Liquids

Reactions were carried out in suspension in benzene, or in solution in chloroform under reflux at temperatures much lower than those used for thermolyses and reactions generally do not go to completion (Table VI).

Reaction of the methyl ester, **A**, under reflux, in chloroform solution did not go to completion but gave the expected phosphonium ion, **2**, the phosphine oxide and the ethyl triphenylphosphonium bromide **3** formed by C-alkylation of the reactive $Ph_3P=CH_2$ by CH_3Br.

Reactions of the ethyl and t-butyl esters, **B** and **D**, as suspensions in benzene under reflux at 80°C, gave only the methyl phosphonium salt, **2** (Table VI). Apparently for the ethyl ester the first formed ylid **1** reacts with HCl or HBr in the solid, and intermediates do not separate. There are no products of transylidation and, depending on conditions, some reactions only go to a limited extent. In these experiments. the overall reactions could be intramolecular or behave as such.

Ylid Trapping

We assume that the initial reaction is formation of the very labile $Ph_3P=CH_2$ which reacts by transylidation, or with other electrophiles, e.g., HX or CH_3X formed in the initial reaction.

Added electrophiles should also trap $Ph_3P=CH_2$, and other ylides, but they have to be sufficiently reactive to compete with starting material, or with products of the initial reaction. The initial products and starting material will diffuse apart very slowly in viscous molten phosphonium salt, which favors their reaction, while an added reagent has to diffuse through this medium before it can trap an intermediate. As a result, only reactive electrophiles, e.g., acyl chlorides, or benzyl bromide, trap $Ph_3P=CH_2$, **1**, in some conditions, but there is no reaction with the less reactive succinic anhydride. Products of the Wittig reaction with intermediate ylidic esters **4** are observed with p-nitrobenzaldehyde, but not with p-methoxybenzaldehyde. This reaction, Eq. (9), confirms the transient existence of these ylidic ester intermediates and the Wittig reaction competes with their spontaneous decomposition to the phosphine oxide.
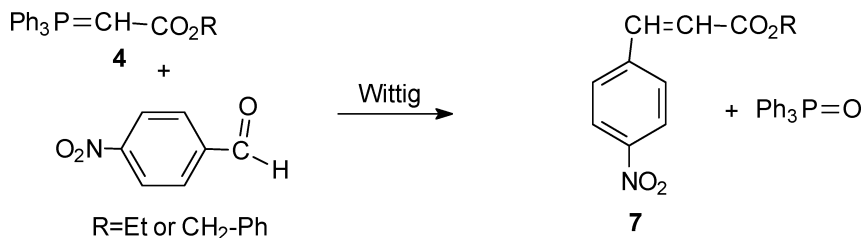
$$(9)$$

TABLE VII a Trapping of Intermediate 1, Ph$_3$P=CH$_2$, by Benzyl Bromide

Ph$_3$P$^+$-CH$_2$- CO$_2$R Br$^-$	Ph-CH$_2$Br (25.2 mmol) $\longrightarrow$	Ph$_3$P$^+$-CH$_3$Br$^-$ + **2**	Ph$_3$P$^+$-CH$_2$-CH$_2$-Ph Br$^-$ **8**	+ Ph$_3$P=O
R=Me, **A** (4.8 mmol)	134°C $\longrightarrow$ 1 At., 1.5 h	29%	51%	20%
R=Et, **B** (4.7 mmol)	142°C $\longrightarrow$ 1 At., 1.5 h	82%	Traces	18%

There was no indication of trapping of Ph$_3$P=CH$_2$ in a Wittig reaction, probably because it reacts very rapidly with HBr or the phosphonium salt.

Trapping results depend on relative amounts of substrate and the trapping agent; if the latter is in significant excess, it can dissolve the substrate, and the reaction intermediates will form in intimate contact with the trapping agent. Then, the reaction will progress as if in an organic medium, with concentrated reagents, rather than as in an ionic liquid.

The competition between the added reagent and an electrophile generated in the initial reaction is illustrated by trapping by benzyl bromide in thermolysis of the methyl and ethyl esters (Table VII). There is extensive trapping by benzyl bromide with the methyl, but almost no trapping with the ethyl, ester. The initial step of decomposition of the methyl ester, **A**, generates MeBr which can escape and does not compete with the stronger alkylating agent, benzyl bromide, for the initially formed Ph$_3$P=CH$_2$. Phenyl ethyl phosphonium salt **8** is generated as the major product, which is identified by ^{1}H NMR spectroscopy and comparison with a standard, (Table VII a). In the reaction of the ethyl ester **B**, HBr is generated adjacent to the ylid and, as an effective electrophile, competes strongly with benzyl bromide by protonating the initially formed ylid. Methylphosphonium salt **2** was formed (82%), isolated by crystallization from CHCl$_3$/AcOEt (3:1) and identified by IR spectroscopy and comparison with a standard (Table VII a). Benzoyl

TABLE VII b Trapping of Thermolysis Intermediate 1, Ph$_3$P=CH$_2$, by Benzoyl Chloride

Ph$_3$P$^+$-CH$_2$-CO$_2$RBr$^-$	Ph-COCl (21.5 mmol) $\longrightarrow$	Ph$_3$P$^+$-CH$_3$Br$^-$ **2**	+ Ph$_3$P$^+$-CH$_2$-CO-Ph Cl$^-$ **9**	+ Ph$_3$P=O
R = CH$_3$, **A** (3.6 mmol)	160°C 1 At.,1h $\longrightarrow$	10%	80%	10%
R = C(CH$_3$)$_3$, **D** (3.5 mmol)	140°C $\longrightarrow$ 1 At., 1.5h	22%	78%	

chloride is a very effective electrophile and its trapping of the first-formed ylid **1** is a significant reaction. Phenacylphosphonium chloride **9** was formed as the main reaction product (Table VII b).

Physical Conditions of the Thermolysis

Reactions were carried at atmospheric or reduced pressure, where generally protonation or methylation of the first formed $Ph_3P=CH_2$ is reduced by increasing the escape of the halogen acid or methyl halide. However, reaction conditions are not reproducible, because they depend on the rate of decomposition, which changes as the medium changes in the course of reaction. In addition isolatable nonvolatile products are derived from both nonvolatile intermediates (Schemes 1 and 2) and volatile species which may escape during reaction.

Reactions in the melt were generally continued until bubbling had apparently ended indicating essentially complete reaction. The reaction medium was not stirred but bubbling generates some mixing.

Carrying out reaction under reduced pressure generally has a major effect on product composition because of escape of some reactive intermediates, especially at the higher temperatures, however, even volatile species such as CH_3X, can remain as bubbles in the viscous melt. The loss of volatile electrophiles apparently depends upon the physical state of the ionic liquid reaction medium. In some experiments small bubbles escaped freely, but sometimes there was little escape until gas built up and large bubbles formed, and the volatiles escaped. Therefore, although changes in the products are usually understandable in these simple terms, we cannot quantify the results.

Formation of Triphenylphosphine Oxide

An intermediate ylidic ester, **4**, can form triphenyl phosphine oxide, probably by transfer of an acyl oxygen to phosphorus. Formation of acetylene derivatives has been observed in other thermolyses and may occur here.[13]
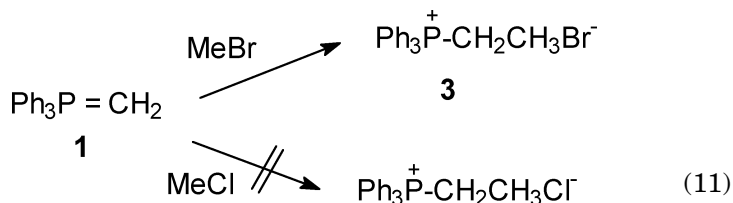

$$\text{(10)}$$
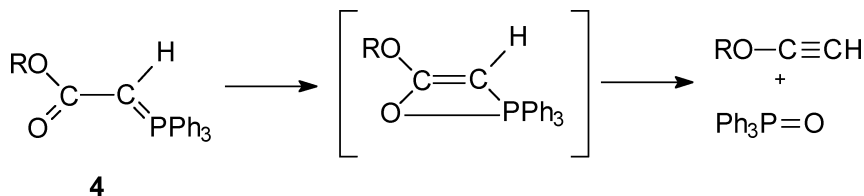
This reaction competes with trapping of the ylid ester by an electrophile, e.g., an activated electrophile.

Decomposition of ylid, **4**, producing triphenylphosphine oxide, was demonstrated in a control reaction: Thermolysis of $Ph_3P=CH-CO_2Et$, **4b**, at $152°C$, 1 At, over 2 h, gave a 16% yield of $Ph_3P=O$ which was isolated and identified by ^1H-NMR and Ir spectroscopy.

The t-butyl ester, **D**, behaves differently from esters of primary and secondary alcohols in giving no phosphine oxide on thermolysis, where the only nonvolatile product is $Ph_3P^+-CH_3X^-$. Ylid, **1,** could be formed but reacts only with the halogen acid, or Ph-COCl, and not by transylidation, which would be sterically hindered by the bulky t-butyl group.

Effect of the Halide Ion

Most experiments were made with the bromide salts, but they and the corresponding chlorides, generally behaved similarly, although thermolysis of the methyl ester is an exception to this generalization because while we assume that the initial reactions generate ylid **1** and the methyl halide, only methyl bromide traps the ylid.

$$Ph_3P=CH_2 \quad \begin{array}{c} \xrightarrow{\text{MeBr}} Ph_3\overset{+}{P}\text{-}CH_2CH_3Br^- \\ \textbf{3} \\ \xrightarrow{\text{MeCl}} \!\!\!\!\!/\!\!/\ Ph_3\overset{+}{P}\text{-}CH_2CH_3Cl^- \end{array} \qquad (11)$$

1

Several factors contribute to this difference, viz. methyl chloride is a weaker methylating agent than the bromide and, being more volatile, should escape more readily.

The situation is more complicated for the ethyl ester because the initially formed halogen acid can trap $Ph_3P=CH_2$, **1**, giving the phosphonium salt, **2**, but transylidation of **1** with the starting material also gives **2** which complicates comparison of the roles of the halide ion in these reactions.

In thermolysis of the chloride and bromide salts of the t-butyl ester, the methyl triphenylphosphonium ion **2** is the only nonvolatile product and we have no evidence regarding the role of the halide ion. As noted, ion pair interaction would favor a concerted fragmentation, as shown in Eq. (6).

Thermal Decomposition of Ylidic Esters

The initial decomposition of the phosphonium esters, possibly excepting the t-butyl ester, forms $Ph_3P=CH_2$ which can be methylated, protonated, or undergo transylidation to give an ylidic ester which decomposes spontaneously. The final major nonvolatile products of decomposition of the methyl, ethyl and isopropyl phosphonium esters are therefore Ph_3PO, $Ph_3P^+\text{-}CH_3X^-$ and, for methyl ester, $Ph_3P^+\text{-}CH_2CH_3X^-$.

Except in a few special cases, the ylidic ester formed by transylidation decomposes thermally giving the phosphine oxide and probably a volatile acetylene derivative (Eq. 5),[13] which, like an alkene, should decolorize bromine. The driving force for this reaction, as in the Wittig reaction, is oxygen transfer to a cationoid phosphorus.

Substituted acetylenes are acids in solution and in the gas phase,[14] and could compete with a halogen acid in protonating ylid **1**. The acetylene derivative should escape readily from the molten reaction medium but may survive long enough to protonate **1**, or other ylides. In that event, the product balance will depend upon the competition between a volatile halogen acid and a transient acetylene derivative formed in the last step of a reaction sequence which may also involve transylidation.

It appears that most intermediate ylidic esters **4** do not survive thermolysis, but although these compounds have sharp melting points, without decomposition, and properties of the molten salts, as ionic liquids, may promote decomposition of the ylidic esters.

Reaction Paths

Some of the reaction steps in thermolysis of the phosphonium esters are chemically similar to other overall fragmentations.[15] The initial decarboxylation is similar to thermal decompositions of carboxylate,[1] xanthate,[2] and protonated amino acid esters,[16] except that the initial reaction gives a transient ylid.

The first formed phosphorus ylid **1** reacts with any available electrophile with proton transfer from a halogen acid, or a phosphonium salt in transylidation, or with alkylation or acylation, and these subsequent reactions may involve added reagents.

Transylidation generates an ylidic ester **4**, which is unstable at the reaction temperatures and generally decomposes to a phosphine oxide and probably a substituted acetylene, in a reaction akin to the Wittig reaction, although reaction with a phosphonium ester can give the thermally stable ylid-phosphonium salt, **5**.[11]

Intermediates in thermolyses of the cationic phosphonium esters should be very short-lived and, in the viscous ionic liquid, tend to react

with their nearest neighbor, which therefore competes effectively with more reactive added reagents.

Reaction of the t-butyl ester does not fit the above generalizations because its thermolysis does not involve transylidation and formation of phosphine oxide.

The reaction paths in these thermolysis are generally similar to those observed in decompositions in solution or suspension, although temperatures differ.

CONCLUSIONS

Products of thermal decompositions of molten salts of triphenylphosphonium esters have been examined. Reactions of methyl, ethyl and isopropyl esters occur with initial formation of $Ph_3P=CH_2$, which can react with the starting material by transylidation, and, for the methyl ester, by reaction with methyl halide formed in the initial reaction, and, for the ethyl and isopropyl esters, by reaction with initially formed halogen acid, but decomposition of the t-butyl ester gives only the methyl phosphonium salt. Ylidic intermediates can be trapped by alkyl and acyl halides and by an activated aldehyde, but the reaction media are viscous ionic liquids and these added electrophiles have to be in sufficient concentration to compete with electrophiles formed in the initial decompositions in contact with the ylides. An important exception to this generalization is that with excess trapping agent it, rather than the molten ester, may become the reaction medium, with considerable trapping of the ylid. Ylidic esters, formed by transylidation, generally decompose intramolecularly giving triphenyl phosphine oxide in the ionic liquid, although isolated esters have sharp melting points. The initial decomposition gives volatile products, which may escape or react with the ylidic intermediates, and overall products depend on pressure. Changes in the anion of the phosphonium ester salt affect product composition. Ions are probably paired in the ionic liquid but changes in product composition are understandable in terms of the nucleophilicity or basicity of the anion and electrophilicity of the undissociated conjugate acid. Products of reaction in chemically inert solvents are similar to those in the molten salts, except for temperature differences and the fact that reactive ionic intermediates mix more freely in moderately polar solvents, e.g., $CHCl_3$, in which reactants are soluble, than in benzene where reaction is in a dispersion of the solid.

Product formation depends on reactant properties and concentrations, but also on physical conditions, and therefore on physical properties which change during the reaction. The reactions that occur in these thermolysis are as expected in terms of the known chemistry

of phosphonium ylides and medium effects on these reactions. Substituents in the alkyl group do not significantly affect the reactions.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Bruker DRX300 spectrometer and were referenced to TMS. IR spectra were recorded on a Bruker IFS 56 FT spectrometer with a KBr disk. Melting points are uncorrected. The thermolysis products were characterized and quantified by comparison of their ^{1}H-NMR spectra in CDCl$_3$ with authentic samples, and concentrations were estimated by signal integration, avoiding signals, which were overlapped. Elemental analyses were performed with a Fisons EA 1108 analyzer to estimate novel compounds described in this work, **Ac**, **E**, **Be**, **8**, and **9**. Benzyl bromoacetate; allyl 2-bromoacetate; trans-ethyl 4-nitrocinnamate, **7**; 2-chloroacetophenone, were commercial samples.

Synthesis

The Synthesis of Alkylester Triphenylphosphonium Salts

A number of these compounds are known and we follow the general procedure[17] illustrated for the synthesis of **methoxycarbonyl methyl triphenylphosphonium bromide**, **A**. An equimolar mixture of triphenyl phosphine and methyl bromoacetate dissolved in the minimum amount of dry benzene, was stirred at room temperature for 4 h to produce a white solid which was removed by suction filtration and washed with benzene. The filtrate and the washed benzene fractions were stirred again at r. t. until no more solid was formed (2–8 h). The dried solid product **A**, yield 97%, m.p., 161–162°C,[18] has ^{1}H NMR (CDCl$_3$)δ_{ppm}: 3.61 (s, 3H, CH$_3$), 5.60 (d, 2H, J= 14 Hz, CH$_2$), 7.66-7.94 (m, 15 H).

The following phosphonium salts were obtained by the above procedure from the appropriate halo derivatives.

Methoxycarbonyl Methyl Triphenylphosphonium Chloride, Ac. M.p. 152–153°C., ^{1}H NMR (CDCl$_3$)δ_{ppm}: 3.60 (s, 3H, CH$_3$), 5.55 (d, 2H, J = 14Hz, CH$_2$), 7.63-7.92 (m, 15 H). Anal. Calcd. for C$_{21}$H$_{20}$ClO$_2$P(371.8):C, 67.83; H, 5.69. Found: C, 67.67; H, 5.50.

Ethoxycarbonyl Methyl Triphenylphosphonium Bromide, B. Yield 97%, m.p. 155-156°C,[18] ^{1}H-NMR (CDCl$_3$)δ_{ppm}: 1.0 (t, 3H, J = 7 Hz, CH$_3$), 4.0 (q, 2H, J= 7 Hz, CH$_2$), 5.5 (d, 2H, J = 14 Hz, CH$_2$), 7.7 (m, 15 H).

Ethoxycarbonyl Methyl Triphenylphosphonium Chloride, Bc. Yield 90%, m.p. 121–122°C,[19] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 1.0 (t, 3H, J = 7 Hz, CH$_3$), 3.99 (q, 2H, J = 7 Hz, CH$_2$), 5.48 (d, 2H, J = 14 Hz, CH$_2$), 7.7 (m, 15 H).

Isopropyloxycarbonyl Methyl Triphenylphosphonium Bromide, C. Yield 94%, m.p. 150–151°C.,[20] ^{1}H NMR(CDCl$_3$)δ_{ppm}: 1.03 (d, 6H, CH$_3$), 4.84 (sept, 1H, J = 6 Hz, CH), 5.50 (d, 2H, J = 14 Hz, CH$_2$), 7.6–8.0 (m, 15 H).

t-Butyloxycarbonyl Methyl Triphenylphosphonium Bromide, D. Yield 96%, m.p. 175–176°C,[21] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 1.22 (s, 9H, CH$_3$), 5.50 (d, 2H, J = 14Hz, CH$_2$), 7.7–8.0 (m, 15H).

t-Butyloxycarbonyl Methyl Triphenylphosphonium Chloride, Dc. Yield 90%, m.p. 169–170°C,[22] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 1.21 (s, 9H), 5.45 (d, 2H, J = 14 Hz, CH$_2$), 7.6–8.0 (m, 15 H).

Benzyloxycarbonyl Methyltriphenyl Phosphonium Bromide, E. This salt was synthesized as above, by reaction of triphenylphosphine with benzyl bromoacetate, yield 84%, m.p. 99–103°C, ^{1}H NMR (CDCl$_3$)δ_{ppm}: 5.03 (s, 2H), 5.69 (d, 2H), 7–8 (m, 20 H). Anal. Calcd. for C$_{27}$H$_{24}$BrO$_2$P (491.4): C, 66.00; H, 4.92. Found: C, 65.71; H, 4.65.

Allyloxycarbonyl Methyl Triphenylphosphonium Bromide, F. This salt was prepared by the general procedure: reaction of triphenylphosphine with allyl 2-bromoacetate, yield 98%, m.p. 129°C,[23] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 4.50 (d, 2H, O-CH$_2$), 5.20 (m, 2H, CH$_2$ =), 5.60 (d, 2H, P$^+$-CH$_2$), 5.75 (m, 1H, -CH=), 7.5–8.0 (m, 15H).

Synthesis of Ethoxycarbonyl Methyl Triphenylphosphonium p-Toluene Sulfonate, Be. This salt was obtained by reaction of Ph$_3$P=CH-CO$_2$CH$_2$-CH$_3$ with equimolar p-toluenesulfonic acid dissolved in a minimum amount of dry benzene and stirred at room temperature A white solid formed immediately. The solid, filtered under vacuum was benzene washed to yield 85% of product **Be**, m.p. 165–166°C, ^{1}H NMR (CDCl$_3$)δ_{ppm}: 1.01 (t, 3H, J = 7 Hz, CH$_3$), 2.29 (s, 3H, CH$_3$), 3.98 (q, 2H, J = 7 Hz, CH$_2$), 5.11 (d, 2H, J = 14 Hz, CH$_2$), 7.04 (d, 2H, J = 8 Hz), 7.64–7.83 (m, 17 H). Anal. Calcd. for C$_{29}$H$_{29}$O$_5$PS (520.6): C, 66.91; H, 5.61. Found: C, 66.60; H, 5.52.

Synthesis of Thermolysis Products as Spectroscopic Standards

Methyl Triphenylphosphonium Bromide, 2. Prepared by the above general procedure, yield 99%, m.p. 230°C,[9] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 3.33 (d, 3H, J = 14 Hz, CH$_3$), 7.6–8.0 (m, 15 H).

Ethyl Triphenylphosphonium Bromide, 3. Prepared as above, yield 90%, m.p. 206–208°C,[9] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 1.36 (d-t, 3H), 3.60 (m, 2H), 7.70 (m, 15H).

3-Ethoxycarbonyl--3--Triphenylphosphoranylidene--2-Oxopropane Triphenyl Phosphonium Bromide, 5a. This ylid-phosphonium salt was obtained by reaction of carbethoxymethylene triphenylphosphorane (1 g, 2.87 mmol) with the phosphonium salt **2** (1.42 g, 3.3 mmol). Yield 57%, m.p. 180–183°C,[11] ^{1}H NMR (CDCl$_3$)δ_{ppm}: 0.57 (t, 3H, J = 7 Hz, CH$_3$), 3.67 (q, 2H, J = 7 Hz, CH$_2$), 5.37 (d, 2H, J = 12.1 Hz, CH$_2$), 7.46–7.82 (m, 30 H).

2-Phenylethyl Triphenylphosphonium Bromide, 8. This compound was prepared by C-alkylation of methylenetriphenylphosphorane[24] with benzyl bromide. Methyl triphenylphosphonium bromide **2** (3.6 g, 0.01 mol) was added cautiously over several minutes to a solution of n-butyl lithium (0.01 mol., approx. 11 ml of the commercially available 22% solution in hexane) in 20 ml of anhydrous ether. The mixture was then stirred at room temperature under N$_2$. After 2 h, benzyl bromide (1.9 g, 0.01 mol) was added dropwise and the mixture was stirred for 8 h and filtered by suction. The solid was ether washed and extracted with chloroform. The organic extract was dried (anhydrous magnesium sulfate), and the solvent was removed under vacuum. The residue was crystallized from CHCl$_3$/AcOEt (1:5) to form **8** (2.9 g, 65%), m.p. 216°C, ^{1}H NMR (CD Cl$_3$)δ_{ppm}: 3.0 (sextuplex, 2H), 4.0 (sextuplex, 2H), 7.0–8.0 (m, 20 H). Anal. Calcd. for C$_{26}$H$_{24}$BrP (447.4): C, 69.81; H, 5.41. Found: C, 69.52; H, 5.38.

Phenacyltriphenylphosphonium Chloride, 9. 2-Chloroacetophenone (15.5 g, 0.1 mol) was added in portions to a chloroform (70 ml.) solution of thiphenylphosphine (26.2 g, 0.1 mol) and was stirred at room temperature for 6 h. The solution was filtered into 0.5 l. of petroleum ether (40-60°C) to produce a precipitate which was collected, dried and crystallized from water. M.p. 275°C. ^{1}H NMR (CDCl$_3$)δ_{ppm}: 6.8 (d, 2H), 7.5-8.0 (m, 20 H). Anal. Calcd. for C$_{26}$H$_{22}$ClOP (416, 9): C, 74.91; H, 5.32. Found: C, 74.71; H, 5.10.

Thermolysis of Triphenylphosphonium Alkyl Ester Salts

General Procedure for Thermolysis at Normal Pressure

The ester-phosphonium salt (4–5 mmol) was heated in a round-bottom flask fitted with a condenser and an internal temperature control. The vertical condenser was modified to allow collection of condensate. At near to the melting point, the thermolysis starts with extensive

bubbling in the viscous melt. Complete reaction is indicated by the end of bubbling (1–2 h).

The crude thermolysis product, is generally a solid at room temperature, and was analyzed by ^{1}H NMR spectroscopy after dissolution in CDCl$_3$, eliminating product discrimination during analysis. Yields are in mole%. Volatile products formed in the thermolysis were studied by connecting the condenser outlet to a bubbler with aqueous solutions of barium hydroxide or silver nitrate, or bromine/CCl$_4$ to detect CO$_2$, HBr$_g$, alkyl halides, or alkenes and acetylenes, respectively.

General Procedure for Thermolysis at Reduced Pressure

The equipment as described was connected to the vacuum system via the condenser. Care had to be taken to avoid spattering of material during thermolysis, and trapping of volatiles was not examined.

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