

# Some new observations on an old reaction: disproportionation and the formation of P-O-P intermediates in the Michaelis-Arbuzov reaction of triaryl phosphites with alkyl halides

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Dedicated to Professor Chengye Yuan on the occasion of his 80<sup>th</sup> birthday and in recognition of his distinguished contributions to organophosphorus chemistry

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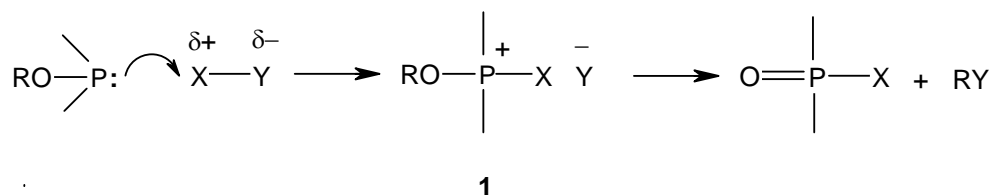
## Abstract

Thermolysis of methyltriaryloxyphosphonium halides (ArO)<sub>3</sub>PMeX (X = Br or I) in the molten state (> 175 °C) was accompanied by disproportionation, with the formation of structures of the general type (ArO)<sub>n</sub>PMe<sub>4-n</sub>X (X = Br or I; n = 0-4). Further decomposition to give the corresponding aryl halides and phosphoryl derivatives became progressively slower as aryloxy groups were replaced by methyl. Thermal decomposition in CDCl<sub>3</sub> (sealed tube) additionally confirmed the formation of novel species containing a P-O-P linkage. Products were identified by a combination of <sup>31</sup>P and <sup>1</sup>H NMR spectroscopy. Possible reaction mechanisms are discussed.

**Keywords:** Michaelis-Arbuzov, quasiphosphonium, disproportionation, NMR spectroscopy

## Introduction

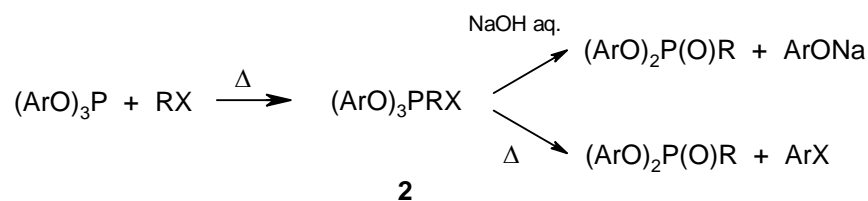
The Michaelis-Arbuzov reaction is one of the best known and most fundamental reactions of organophosphorus chemistry encompassing, in its widest aspects, all reactions of phosphorus (III) esters with electrophilic reagents. The reaction proceeds via an alkoxy- or aryloxyphosphonium intermediate **1**, leading to the formation of a tetrahedral P(V) product containing a P=O bond (Scheme 1).<sup>1</sup>



**Scheme 1**

The applications of this type of reaction in the synthesis of phosphonates, phosphinates, and phosphine oxides are legion<sup>2</sup> and include methods for the synthesis of a wide range of useful organophosphorus compounds. Recent examples include the synthesis of  $\alpha$ -aminophosphonates by the interaction of phosphite esters with *N*-substituted trifluoroacetimidoyl chlorides.<sup>3</sup>

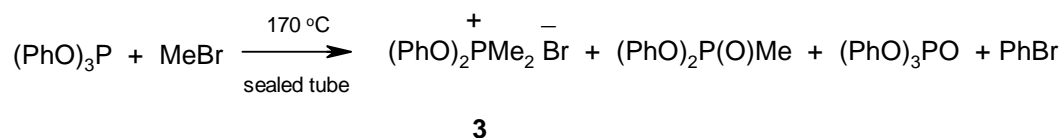
Some of the earliest examples involved the reactions of triaryl phosphites with alkyl halides, giving 1:1 adducts, the so-called quasiphosphonium salts **2**, which on hydrolysis or thermolysis yielded the corresponding diaryl alkylphosphonates (Scheme 2).<sup>4</sup>



### Scheme 2

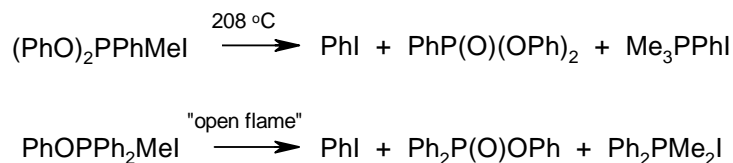
<sup>31</sup>P NMR spectroscopic studies and single crystal X-ray diffraction measurements have confirmed that the adducts **2**, and many other similar intermediates derived from both aryl and alkyl P(III) esters, are true phosphonium salts rather than pentacoordinate species.<sup>5-8</sup> Examples of the latter are rare but have been detected in certain special cases such as the reactions of ethyl *o*-phenylene phosphite with halogens or phenylsulfenyl chloride at low temperatures.<sup>9</sup>

In the course of structural and spectroscopic studies of quasiphosphonium salts we prepared the methyl bromide and methyl iodide adducts of triphenyl phosphite (**2**, Ar = Ph, R = Me, X = Br or I) by heating the reactants together at 90-100 °C.<sup>5</sup> We also found that extended periods of heating at higher temperatures (up to 170 °C in a sealed tube) led to the isolation of the unexpected dimethyldiphenoxyphosphonium bromide **3** (18% yield), together with diphenyl methylphosphonate, triphenyl phosphate, and bromobenzene (Scheme 3).<sup>7</sup>



### Scheme 3

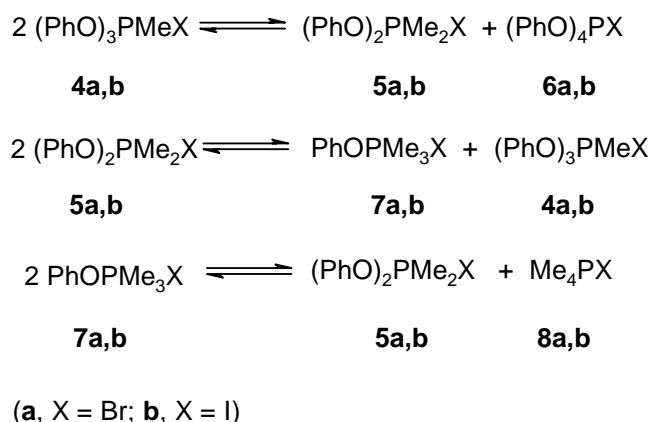
This result was reminiscent of the disproportionations reported by Nesterov who found that thermal decomposition of the methyl iodide adducts of diphenyl phenylphosphonite and phenyl diphenylphosphinite above 200 °C yielded phosphonates devoid of methyl substituents (Scheme 4).<sup>10</sup>

**Scheme 4**

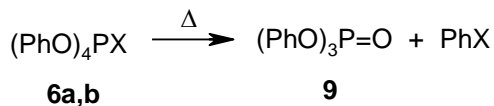
No other examples of the redistribution of aryloxy and methyl groups at phosphorus in the course of Michaelis-Arbuzov reactions appear to have been reported. We have therefore monitored the thermal decomposition of selected quasiphosphonium salts by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy<sup>11,12</sup> and we present our results and conclusions below.

## Results and Discussion

Although the initial formation of a 1:1 complex **2** between a triaryl phosphite and methyl bromide or methyl iodide (Scheme 2) occurs readily at 100 °C, further reaction to give the aryl halide and phosphonate ester requires significantly higher temperatures. Under these conditions other competing reactions, not previously generally recognized, may occur. Thus, we have found that the thermal decomposition of methyltriphenoxyphosphonium bromide **4a** or iodide **4b** in the molten state at 175 °C, or higher, is accompanied by the formation of disproportionation products (Scheme 5), identified by a combination of  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy (Tables 1 and 2, and Experimental Section); and similar results were obtained by the thermolysis of dimethyldiphenoxyphosphonium bromide **5a** or iodide **5b**.

**Scheme 5**

Only the tetraphenoxyphosphonium species **6a** or **6b** were not detectable directly but these are the least stable and presumably undergo dearylation relatively quickly to give triphenyl phosphate **9** (Scheme 6).



## Scheme 6

**Table 1.** Thermal decomposition of methyltriphenoxyphosphonium bromide **4a** (no solvent)<sup>a</sup>

Time/h	Temp/°C	(PhO) <sub>3</sub> PMeBr <sup>b</sup>	(PhO) <sub>2</sub> PMe <sub>2</sub> Br <sup>c</sup>	PhOPMe <sub>3</sub> Br <sup>d</sup>	(PhO) <sub>2</sub> P(O)Me <sup>e</sup>	PhOP(O)Me <sub>2</sub> <sup>f</sup>
48	175	67.8	16.0	-	16.1	-
96	175	52.3	22.3	-	25.4	-
120	175	44.8	25.2	1.2	28.8	-
192	175	28.4	29.0	2.6	40.0	-
240	175	14.6	20.5	3.6	61.2	-
120	210	-	11.5	7.7	76.9	3.8
280	175-250	-	1.7	9.2	78.1	9.4 <sup>g</sup>

<sup>a</sup> Table shows mole % composition of MeP compounds (phosphonium salts and phosphonates) present, based on integration of the methyl proton signals. <sup>b</sup>  $\delta_{\text{H}}$  3.26 (d,  $^2J_{\text{PCH}} = 17.4$  Hz),  $\delta_{\text{P}}$  41.8 (q). <sup>c</sup>  $\delta_{\text{H}}$  2.88 (d,  $^2J_{\text{PCH}} = 15.0$  Hz),  $\delta_{\text{P}}$  96.2 (septet). <sup>d</sup>  $\delta_{\text{H}}$  2.42 (d,  $^2J_{\text{PCH}} = 14.5$  Hz),  $\delta_{\text{P}}$  102.0 (decet). <sup>e</sup>  $\delta_{\text{H}}$  1.62 (d,  $^2J_{\text{PCH}} = 17.4$  Hz),  $\delta_{\text{P}}$  23.8 (quartet). <sup>f</sup>  $\delta_{\text{H}}$  1.48 (d,  $^2J_{\text{PCH}} = 14.4$  Hz),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 54.5 (septet). <sup>g</sup> (PhO)<sub>3</sub>PO,  $\delta_{\text{P}}$  -17.6, and (PhO)<sub>3</sub>P,  $\delta_{\text{P}}$  127.8 (trace), also present. (All nmr data in CDCl<sub>3</sub>).

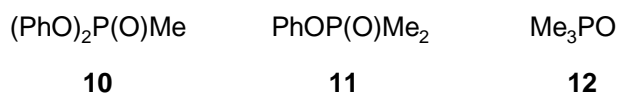
**Table 2.** Thermal decomposition of methyltriphenoxyphosphonium iodide **4b** (no solvent)<sup>a</sup>

Time/h	Temp/°C	(PhO) <sub>3</sub> PMeI <sup>b</sup>	(PhO) <sub>2</sub> PMe <sub>2</sub> I <sup>c</sup>	PhOPMe <sub>3</sub> I <sup>d</sup>	Me-P-O-P <sup>e</sup>	(PhO) <sub>2</sub> P(O)Me <sup>f</sup>
24	175	75.6	12.0	-	3.6	8.8
48	175	63.4	18.9	-	4.1	13.6
120	175	43.0	25.3	-	3.2	28.5
192	175	24.7	35.3	-	-	35.3
48	210	3.9	11.3	14.8	-	70.0 <sup>g</sup>
22	190-230	-	4.4	9.3	-	86.3 <sup>h</sup>

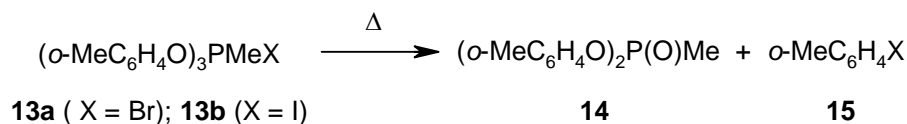
<sup>a</sup> Table shows mole % composition of MeP compounds (phosphonium salts and phosphonates) present, based on integration of the methyl proton signals. <sup>b</sup>  $\delta_{\text{H}}$  3.05 (d,  $^2J_{\text{PCH}} = 17.4$  Hz),  $\delta_{\text{P}}$  40.8 (quartet). <sup>c</sup>  $\delta_{\text{H}}$  2.77 (d,  $^2J_{\text{PCH}} = 15.0$  Hz),  $\delta_{\text{P}}$  94.1 (septet). <sup>d</sup>  $\delta_{\text{H}}$  2.35 (d,  $^2J_{\text{PCH}} = 14.0$  Hz),  $\delta_{\text{P}}$  100.7 (decet). <sup>e</sup>  $\delta_{\text{H}}$  2.15 (dd,  $^2J_{\text{PCH}} = 15.6$  Hz) (see later for further characterization of this species). <sup>f</sup>  $\delta_{\text{H}}$  1.65 (d,  $^2J_{\text{PCH}} = 17.7$  Hz),  $\delta_{\text{P}}$  23.9 (quartet). <sup>g</sup> (PhO)<sub>3</sub>PO,  $\delta_{\text{P}}$  -17.0, and (PhO)<sub>3</sub>P,  $\delta_{\text{P}}$  124.4 (trace) also present. <sup>h</sup> Me<sub>4</sub>PI (trace),  $\delta_{\text{P}}$  23.2 (m), possibly present. (All nmr data in CDCl<sub>3</sub>).

The thermal stability of quasiphosphonium salts increases significantly as aryloxy is replaced by methyl. Consequently, apart from triphenyl phosphate **9** and diphenyl methanephosphonate

**10**, the other possible Arbuzov products, viz. phenyl dimethylphosphinate **11** and trimethylphosphine oxide **12** were obtained in relatively small amounts.

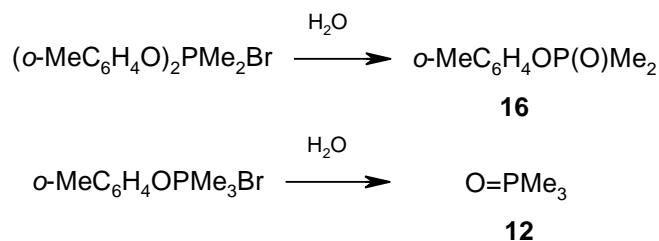


Methyltri-*o*-tolylxyphosphonium bromide **13a** and iodide **13b** underwent disproportionation to a lesser extent when heated at 200 °C, the principal products being di-*o*-tolyl methanephosphonate **14** and the corresponding *o*-halogenotoluene **15** (Scheme 7).<sup>13</sup>



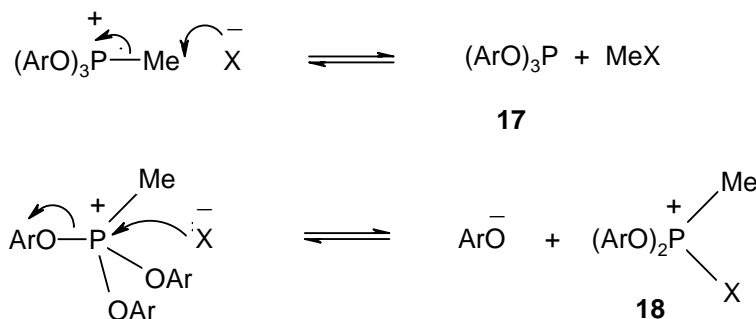
### Scheme 7

However, detection of the hydrolysis products, *o*-tolyl dimethylphosphinate **16** and trimethylphosphine oxide **12**, after exposure of the total products obtained by the pyrolysis of **13a** to moisture (Scheme 8), showed that the transfer of two or of three methyl groups to phosphorus had occurred to some extent.



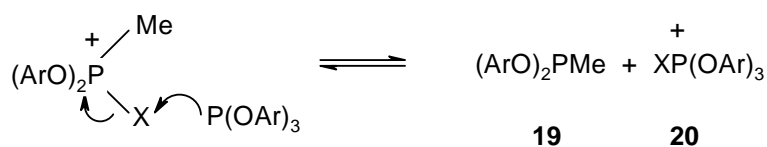
### Scheme 8

The mechanism by which the methyltriaryloxyphosphonium halides undergo disproportionation is considered to be different from that reported some years ago for the related triphenoxy(halogeno)phosphonium halides, (ArO)<sub>3</sub>PX<sub>2</sub>, obtained by the addition of halogen to triaryl phosphite. In these cases, disproportionation occurs relatively easily to give species of the general formula (ArO)<sub>n</sub>PX<sub>5-n</sub> or [(ArO)<sub>x</sub>PX<sub>4-x</sub>]<sup>+</sup>[(ArO)<sub>y</sub>PX<sub>6-y</sub>]<sup>-</sup> and can readily be explained by anionic dissociation of the ligands (phenoxide or halide) and their re-association with phosphorus.<sup>14</sup> However, in the present examples, the involvement of free methyl carbanions is implausible. We propose, therefore, a sequence of bimolecular processes, initiated by nucleophilic attack of halide ion either on carbon (to give the phosphite ester **17**) or on phosphorus to give the halogenophosphonium ion **18** (Scheme 9).

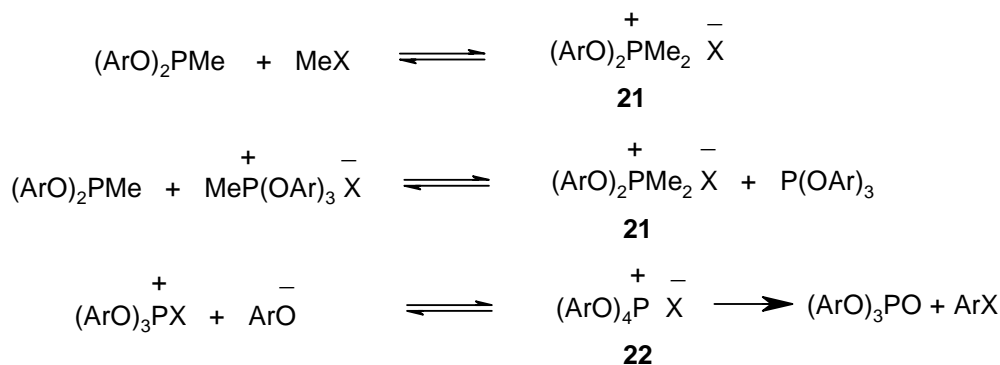


Scheme 9

Transfer of halogen from **18** to **17** will then give the diaryl methylphosphonite **19** and triaryloxy(halogeno)phosphonium ion **20** (Scheme 10), from which the disproportionation products **21** and **22** can readily be formed as shown (Scheme 11).



Scheme 10



Scheme 11

Similar sequences can account for the further exchange of methyl and aryloxy groups, leading to structures of the general type  $(\text{ArO})_n\text{PMe}_{4-n}\text{X}$ .

During the thermal decomposition of molten methyltriphenoxyphosphonium iodide **4b** (Table 2), we also observed the initial formation and subsequent decomposition of a small amount (*ca.* 4 mol %) of an intermediate containing the Me-P-O-P structure. This intermediate became much more evident if the decomposition was carried out in  $\text{CDCl}_3$  (8-10 % w/v solution, sealed tube) and was observed under these conditions as a major feature in the thermolysis of all four quasiphosphonium halides **4a**, **4b**, **13a**, and **13b**, rising to a maximum concentration of 40-50 mol % in some cases but ultimately disappearing with the formation of the normal Arbuzov

product **10** or **14**, together with triaryl phosphate. Typical results are shown for the bromides **4a**, **13a** in Tables 3 and 4.

**Table 3.** Thermal decomposition of methyltriphenoxyphosphonium bromide **4a** in CDCl<sub>3</sub> (8% w/v solution) at 125 – 175 °C<sup>a</sup>

Time/h		Temp/°C	(PhO) <sub>3</sub> PMeBr <sup>d</sup>	(PhO) <sub>2</sub> PMe <sub>2</sub> Br <sup>e</sup>	Me-P-O-P <sup>f</sup>	(PhO) <sub>2</sub> P(O)Me <sup>g</sup>
Period <sup>b</sup>	Total <sup>c</sup>					
15.5	15.5	125	75.3	-	24.7	-
21.5	37.0	125	66.3	-	33.7	-
23.0	60.0	125	61.2	-	38.8	-
18.5	78.5	150	72.9	-	23.5	3.6
19.0	97.5	150	71.4	-	23.5	5.0
46.5	144.0	175	30.5	20.8	31.6	17.0
43.0	187.0	175	20.0	26.8	21.6	31.5
88.5	275.5	175	10.3	26.9	12.0	50.8
98.0	373.5	175	trace	26.8	-	73.2 <sup>h</sup>

<sup>a</sup> Table shows mole % composition of Me-P compounds (phosphonium salts and phosphonates) present, based on integration of the methyl proton signals. <sup>b</sup> Successive periods of heating at the specified temperatures. <sup>c</sup> Overall time of heating. <sup>d</sup> δ<sub>H</sub> 3.22 (d, <sup>2</sup>J<sub>PCH</sub> = 17.4 Hz), δ<sub>P</sub> 43.2. <sup>e</sup> δ<sub>H</sub> 2.74 (d, <sup>2</sup>J<sub>PCH</sub> = 14.4 Hz), δ<sub>P</sub> 95.8. <sup>f</sup> 2.15 (dd, <sup>2</sup>J<sub>PCH</sub> = 14.4 Hz, <sup>4</sup>J<sub>POPCH</sub> ~2 Hz), δ<sub>P</sub> 34.0 (d, J<sub>POP</sub> 30.0 Hz), 77.4 (dq, J<sub>POP</sub> 30.0 Hz, <sup>2</sup>J<sub>PCH</sub> = 14.7 Hz). <sup>g</sup> δ<sub>H</sub> 1.75 (d, <sup>2</sup>J<sub>PCH</sub> = 17.7 Hz), δ<sub>P</sub> 23.6. <sup>h</sup> (PhO)<sub>3</sub>PO, δ<sub>P</sub> -18.0 also present (*ca.* 16 mole % of total phosphorus compounds).

**Table 4.** Thermal decomposition of methyltri-*o*-tolylxyphosphonium bromide **13a** in CDCl<sub>3</sub> (10 % w/v solution) at 200 °C<sup>a</sup>

Time/h	( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> PMeBr <sup>b</sup>	Me-P-O-P <sup>c</sup>	( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> P(O)Me <sup>d</sup>
1.0	82.0	18.0	-
2.25	68.4	23.7	7.9
8.75	29.3	36.6	34.1
21.75	9.1	54.5	36.4
44.0	-	-	99.0 <sup>e</sup>

<sup>a</sup> Table shows mole % composition of MeP compounds (phosphonium salts and phosphonates) present based on integration of the methyl proton signals. <sup>b</sup> δ<sub>H</sub> 3.27 (MeP, d, <sup>2</sup>J<sub>PCH</sub> = 15.8 Hz), 2.16 (s, *o*-Me). <sup>c</sup> δ<sub>H</sub> 2.38 (dd, <sup>2</sup>J<sub>PCH</sub> = 13.0 Hz, <sup>4</sup>J<sub>POPCH</sub> ~2 Hz), 2.00 (s, *o*-Me) and 2.10 (s, *o*-Me), <sup>d</sup> δ<sub>H</sub> 1.77 (MeP, d, <sup>2</sup>J<sub>PCH</sub> = 17.4 Hz), 2.25 (s, *o*-Me). <sup>e</sup> Also δ<sub>H</sub> 2.36 (s, *o*-MeC<sub>6</sub>H<sub>4</sub>Br).

The iodides **4b**, **13b** behaved similarly (see Tables 5 and 6), although the reactions were not forced to completion in these cases as dark brown tarry by-products were formed at higher temperatures.

**Table 5.** Thermal decomposition of methyltriphenoxyphosphonium iodide **4b** in CDCl<sub>3</sub> (8 % w/v solution) at 125 °C<sup>a</sup>

Time/h	(PhO) <sub>3</sub> PMeI <sup>b</sup>	(PhO) <sub>2</sub> PMe <sub>2</sub> I <sup>c</sup>	Me-P-O-P <sup>d</sup>	(PhO) <sub>2</sub> P(O)Me <sup>e</sup>
12	70.7	-	9.1	20.2
42	47.0	-	22.5	30.5
103	39.9	-	20.8	39.3

<sup>a</sup> Table shows mole % composition of MeP compounds (phosphonium salts and phosphonates) present based on integration of the methyl proton signals. <sup>b</sup>  $\delta_{\text{H}}$  3.12 (d,  $^2J_{\text{PCH}} = 16.8$  Hz). <sup>c</sup> Not detectable. <sup>d</sup>  $\delta_{\text{H}}$  2.15 (dd,  $^2J_{\text{PCH}} = 14.4$  Hz,  $^4J_{\text{POPCH}} \sim 2$  Hz), <sup>e</sup>  $\delta_{\text{H}}$  1.75 (d,  $^2J_{\text{PCH}} = 17.7$  Hz).

**Table 6.** Thermal decomposition of methyltri-*o*-tolylxyphosphonium iodide **13b** in CDCl<sub>3</sub> (8 % w/v solution) at 200 °C<sup>a</sup>

Time/h	( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> O) <sub>3</sub> PMeI <sup>b</sup>	( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> PMe <sub>2</sub> I <sup>c</sup>	Me-P-O-P <sup>d</sup>	( <i>o</i> -MeC <sub>6</sub> H <sub>4</sub> O) <sub>2</sub> P(O)Me <sup>e</sup>
2.0	35.7	-	47.2	17.6
4.0	24.1	-	51.7	24.0
6.0	15.2	-	54.5	30.3

<sup>a</sup> Table shows mole % composition of MeP compounds (phosphonium salts and phosphonates) present based on integration of the methyl proton signals. <sup>b</sup>  $\delta_{\text{H}}$  3.17 (d,  $^2J_{\text{PCH}} = 15.9$  Hz). <sup>c</sup> Not detectable. <sup>d</sup>  $\delta_{\text{H}}$  2.28 (dd,  $^2J_{\text{PCH}} = 14.0$  Hz,  $^4J_{\text{POPCH}} \sim 2$  Hz), <sup>e</sup>  $\delta_{\text{H}}$  1.81 (d,  $^2J_{\text{PCH}} = 18.0$  Hz).

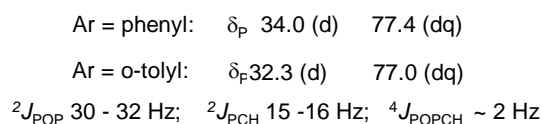
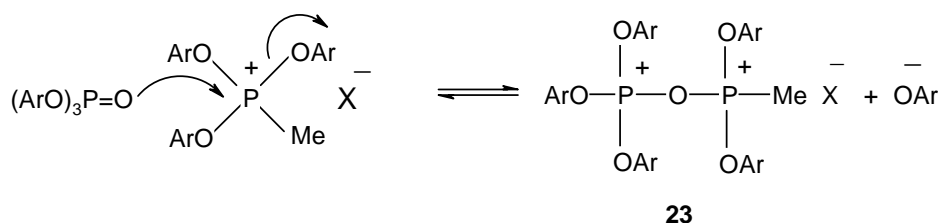
In the case of methyltri-*o*-tolylxyphosphonium bromide **13a**, the P-O-P intermediate was isolated in the form of white crystals from the residue obtained after heating the molten compound (200 °C) in a distillation apparatus and removing volatile by-products under reduced pressure (see Experimental). Although unstable on storage *in vacuo*, this intermediate was sufficiently stable in solution (CDCl<sub>3</sub>) for analysis by NMR spectroscopy, which confirmed the results already deduced from NMR studies of the total reaction products derived from both the phenyl and *o*-tolyl systems during thermal decomposition in CDCl<sub>3</sub>, viz. that intermediate **23** was formed by nucleophilic attack of triaryl phosphate on the quasiphosphonium salt (Scheme 12).

Two differently substituted phosphorus atoms were clearly present ( $\delta_{\text{P}}$  32.3 and 77.0 ppm) with a coupling constant (*ca.* 32 Hz) indicative of an anhydride (P-O-P) structure.<sup>15</sup> One of the phosphorus atoms only (that at lower field) carried a methyl group, giving rise to a doublet of quartets in the proton-coupled spectrum ( $J_{\text{PCH}}$  16.0 Hz,  $J_{\text{POPCH}} \sim 2$  Hz), whereas the other remained as a simple doublet. Closely similar NMR parameters were observed for both the



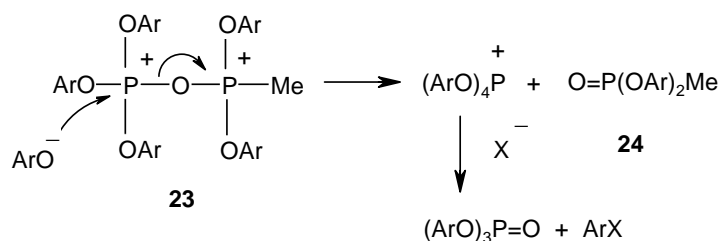
phenyl and tolyl compounds. Integration of the *o*-methyl protons of the isolated *o*-tolyl derivative confirmed the presence of two different types of phosphorus-bonded *o*-tolyl group ( $\delta_{\text{H}}$  2.02 and 2.18, both doublets, with  $^5J_{\text{PH}} = 0.9$  Hz) in 3:2 ratio, in agreement with formulation **23**.

The origin of the triaryl phosphate involved (Scheme 12) is uncertain. In part it may result from disproportionation (Scheme 11) although the absence of equivalent quantities of the corresponding dimethyl substituted disproportionation products **21** suggests that it is also an oxidation product resulting from the interaction of triaryl phosphite, produced by dissociation (Scheme 9), with adventitious oxygen. Such a process would be relatively more significant in a sealed tube in dilute solution than for the neat compound, as observed.



### Scheme 12

Intermediate **23** is of interest in that it suggests the possibility of an alternative route to the formation of the Arbuzov product **24** (Scheme 13), involving dearylation via the more reactive tetra-aryloxyphosphonium species and the regeneration of triaryl phosphate, in which case the latter could be acting catalytically.<sup>16</sup>



### Scheme 13

It is perhaps surprising that we detected none of the analogous P-O-P species which would have been formed by the attack of phosphonate **10** or **14** on the quasiphosphonium ion. Such an intermediate,  $\text{Me}(\text{ArO})_2\text{P}^+(\text{O})\text{OP}^+(\text{O})(\text{OAr})_2\text{Me}$ , being symmetrical, would exhibit only a single

peak in the  $^{31}\text{P}$  NMR spectrum and would therefore be less conspicuous. However, we did not observe significant amounts of any unidentified species during the course of the reaction.

## Experimental Section

**General Procedures.** Because of the sensitivity to moisture of the phosphonium salts under investigation, and of the phosphites to oxidation, all transfers were made in an atmosphere of dry nitrogen.

**Starting materials.** Triphenyl phosphite was obtained commercially and redistilled, b.p.  $172\text{ }^{\circ}\text{C}$  at  $0.5\text{ mmHg}$ ,  $\delta_{\text{P}}$  125 ppm. Tri-*o*-tolyl phosphite,<sup>17</sup> b.p.  $160\text{-}162\text{ }^{\circ}\text{C}$  at  $0.01\text{ mmHg}$ ,  $\delta_{\text{P}}$  130.7 ppm, was prepared by a standard procedure<sup>18</sup> from redistilled *o*-cresol, phosphorus trichloride, and pyridine in light petroleum (b.p.  $30\text{-}40\text{ }^{\circ}\text{C}$ ). Methyl iodide was dried ( $\text{Na}_2\text{SO}_4$ ) and redistilled, b.p.  $43\text{ }^{\circ}\text{C}$ . Methyl bromide was used directly from glass ampoules, as supplied. Acetone (AnalaR grade) was heated under reflux with potassium permanganate and redistilled, b.p.  $56\text{ }^{\circ}\text{C}$ . Anhydrous diethyl ether and petroleum spirit (b.p.  $30\text{-}40\text{ }^{\circ}\text{C}$ ) were stored over sodium wire. Chloroform (AnalaR grade) was redistilled (b.p.  $61\text{ }^{\circ}\text{C}$ ) from phosphorus pentoxide. Deuteriochloroform was stored over molecular sieves.

**Analytical methods.** Elemental analysis (C, H, N) was carried out on a Perkin-Elmer 240 instrument. Halogens (Br or I) were determined by Volhard titration after dissolving the sample in aqueous potassium hydroxide (2% w/v, 100 mL) and acidification of the solution with nitric acid (2M, 25 mL). Phosphorus was determined by digestion of the sample for 10-20 h (Kjeldahl flask) in concentrated sulfuric acid (10 mL) containing selenium catalyst, followed by further heating with concentrated nitric acid (10 mL) until nitrous fumes were no longer evolved. The solution was then carefully diluted, made alkaline by the addition of 0.88 ammonia, and then just acidified (HCl). The so-formed inorganic phosphate was precipitated and weighed as magnesium ammonium phosphate hexahydrate by standard gravimetric procedure.

**Spectroscopy.**  $^1\text{H}$  NMR spectra were recorded on a Perkin-Elmer R12B 60 MHz instrument.  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were obtained on a Bruker WP80 spectrometer operating at 20.12 MHz or 32.395 MHz, respectively. Chemical shifts are reported downfield from TMS (internal standard) for  $^1\text{H}$  and  $^{13}\text{C}$  spectra and from 85% phosphoric acid (external standard) for  $^{31}\text{P}$  spectra. Quantitative data are based on the integration of proton NMR signals.

**Gas chromatography.** Volatile products (containing *o*-bromotoluene) were analyzed at  $115\text{ }^{\circ}\text{C}$  on a  $5\text{ m} \times 1\text{ cm}$  glass column containing 10% PEGA on Celite (60-80 mesh), with  $\text{N}_2$  carrier gas (inlet pressure 17 psi; flow-rate 20 mL/min) and a flame-ionization detector (Perkin-Elmer F11 apparatus).

**Preparation of methyltriphenoxyphosphonium bromide (4a).**<sup>4,6</sup> Triphenyl phosphite (21.6 g, 69.6 mmol) and methyl bromide (9.7 g, 102 mmol) were mixed under dry conditions at  $-80\text{ }^{\circ}\text{C}$ ,

sealed in a thick-walled glass ampoule, and heated at 100 °C for 50 h. The white crystalline product was washed thoroughly with anhydrous ether and dried *in vacuo* to give methyltriphenoxyphosphonium bromide **4a** (25.7 g, 91%), m.p. 155-158 °C (sealed tube),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.24 (Me, d,  $^2J_{\text{PCH}} = 17.4$  Hz), 7.35 (phenoxy, s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 10.1 (Me, d,  $^1J_{\text{PC}} = 127.0$  Hz), 120.4 (d,  $J_{\text{PC}} = 4.3$  Hz), 128.4 (d,  $J_{\text{PC}} = 1.2$  Hz), 131.3 (d,  $J_{\text{PC}} = 1.2$  Hz), 148.8 (d,  $J_{\text{POC}} = 10.4$  Hz) (Ar);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 41.8 (quartet). Anal. Calcd. for C<sub>19</sub>H<sub>18</sub>BrO<sub>3</sub>P: Br, 19.7. Found: Br, 19.6.

**Preparation of methyltriphenoxyphosphonium iodide (4b).**<sup>3</sup> Triphenyl phosphite (16.7 g, 53.9 mmol) and methyl iodide (11.3 g, 79.6 mmol) were heated under reflux (16 h at 86-90 °C) in the absence of moisture. The crude product (25.3 g, 104%), which crystallized slowly (2 h), was washed thoroughly with anhydrous ether and dried *in vacuo* to give methyltriphenoxyphosphonium iodide **4b** as white needle-like crystals, m.p. 115 °C (sealed tube),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 3.12 (Me, d,  $^2J_{\text{PCH}} = 16.8$  Hz), 7.44 (phenoxy, s). Recrystallization of a portion (3.8 g) from anhydrous acetone and diethyl ether gave the product as cream-coloured crystals (2.2 g, 57.9%), m.p. 115 °C (sealed tube),  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 10.9 (Me, d,  $^1J_{\text{PC}} = 127.5$  Hz), 120.2 (d,  $J_{\text{PC}} = 4.1$  Hz), 128.1 (d,  $J_{\text{PC}} = 1.4$  Hz), 131.2 (s), 148.5 (d,  $^2J_{\text{POC}} = 10.2$  Hz) (Ar);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 40.9 (quartet). Anal. Calcd. for C<sub>19</sub>H<sub>18</sub>IO<sub>3</sub>P: I, 28.1. Found: I, 28.0.

**Preparation of methyltri-*o*-tolylxyphosphonium bromide (13a).** Tri-*o*-tolyl phosphite (15.4 g, 43.8 mmol) and methyl bromide (8.1 g, 85.3 mmol) were heated together in a sealed glass ampoule (100 °C) for 32 h. The solid product was washed with anhydrous ether and dried *in vacuo* to give methyltri-*o*-tolylxyphosphonium bromide **13a** (13.5 g, 69.3%) as a white crystalline solid, m.p. 184-187 °C (sealed tube),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.19 (*o*-Me, s), 3.26 (MeP, d,  $^2J_{\text{PCH}} = 15.8$  Hz), 7.33 (Ar, s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 10.9 (MeP, d,  $^1J_{\text{PC}} = 125.4$  Hz), 16.2 (*o*-Me, s), 119.6 (d,  $J_{\text{PC}} = 2.7$  Hz), 128.3-129.3 (m), 133.1 (s), 147.9 (d,  $J_{\text{POC}} = 10.2$  Hz) (Ar);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 42.1 (quartet). Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>BrO<sub>3</sub>P: C, 59.1; H, 5.4; Br, 17.9; P, 6.9. Found: C, 60.0, H, 6.6; Br, 17.8; P, 6.4.

**Preparation of methyltri-*o*-tolylxyphosphonium iodide (13b).** Tri-*o*-tolyl phosphite (5.2 g, 14.8 mmol) and methyl iodide (3.2 g, 22.5 mmol) were heated in a sealed tube (100 °C) for 20 h. The mixture solidified on cooling, was washed with anhydrous ether and dried *in vacuo* to give yellow crystals (5.0 g), m.p. 140-148 °C (sealed tube). Recrystallization from acetone-chloroform (1:1) and ether gave white crystalline methyltri-*o*-tolylxyphosphonium iodide **13b** (3.5 g, 50%), m.p. 155-157 °C (sealed tube),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.20 (*o*-Me, s), 3.16 (MeP, d,  $^2J_{\text{PCH}} = 15.9$  Hz), 7.32 (Ar, s);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 11.9 (MeP, d,  $^1J_{\text{PC}} = 127.0$  Hz), 16.3 (*o*-Me, s), 119.5 (d,  $J_{\text{PC}} = 3.1$  Hz), 128.3-129.2 (m), 133.1 (s), 147.7 (d,  $J_{\text{POC}} = 10.4$  Hz) (Ar);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 41.3 (quartet). Anal. Calcd. for C<sub>22</sub>H<sub>24</sub>IO<sub>3</sub>P: C, 53.5; H, 4.9; I, 25.7; P, 6.4. Found: C, 52.5, H, 5.0; I, 25.6; P, 5.7.

**Thermal decomposition of methyltriphenoxyphosphonium halides in the absence of solvent.** Quantities (*ca.* 0.1 – 0.2 g) of methyltriphenoxyphosphonium bromide **4a**, or iodide **4b**, were heated, without solvent, in sealed glass tubes (175- 250 °C) for the specified periods of

time. Products were dissolved on  $\text{CDCl}_3$  and analyzed by a combination of  $^1\text{H}$  and  $^{31}\text{P}$  NMR (Tables 1 and 2, respectively).

**Thermal decomposition of methyltri-*o*-tolylxyphosphonium halides in the absence of solvent.** Methyltri-*o*-tolylxyphosphonium bromide **13a** or iodide **13b** (*ca.* 0.1 – 0.2 g), were heated (200 °C) in sealed tubes and the products were analyzed as above.

(a) During 21 h at 200 °C the bromide **13a** underwent 75 % decomposition to give di-*o*-tolyl methanephosphonate **14**,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.80 (MeP, d,  $^2J_{\text{PCH}} = 17.4$  Hz), 2.23 (*o*-Me, s),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 23.5 (quartet), and *o*-bromotoluene,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.34 (s). After 38.5 h, followed by exposure of the contents of the tube to atmospheric moisture for 3 days, the detection of small amounts of *o*-tolyl dimethylphosphinate **16**,  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 55.8, and  $\text{Me}_3\text{PO}$ ,  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 74.3, showed that the transfer of two or of three methyl groups to phosphorus had occurred.

(b) The iodide **13b** similarly underwent 80% decomposition in 6 h at 200 °C, giving di-*o*-tolyl methanephosphonate **14**,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.81 (MeP, d,  $^2J_{\text{PCH}} = 18.0$  Hz), 2.25 (*o*-Me, s), *o*-iodobenzene,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.41 (Me, s), and a minor by-product (2 mole %),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.00 (Me, s).

**Isolation of dimethyldiphenoxyphosphonium bromide (5a).**<sup>7</sup> Methyltriphenoxyphosphonium bromide **4a** (4.3 g, 10.6 mmol) was heated alone (molten) in a sealed glass tube (175 °C) for 7 days. After cooling and the removal of volatiles (bromobenzene,  $\delta_{\text{H}}$  7.1-7.6 ppm) under reduced pressure, the solid residue was washed with anhydrous ether and dissolved in acetone-chloroform (1:4). The addition of anhydrous ether caused crystallization of the crude product (1.0 g),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.95 (Me, d,  $^2J_{\text{PCH}} = 15.0$  Hz), containing minor amounts of  $(\text{PhO})_3\text{PMeBr}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 3.24 (Me, d,  $^2J_{\text{PCH}} = 17.4$  Hz), and  $\text{PhOPMe}_3\text{Br}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.66 (Me, d,  $^2J_{\text{PCH}} = 14.0$  Hz). Further washing with hot acetone, followed by recrystallization from chloroform and ether, gave dimethyldiphenoxyphosphonium bromide **5a** (0.6 g, 1.83 mmol, 34%), m.p. 200-210 °C (sealed tube),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.95 (Me, d, 6H,  $^2J_{\text{PCH}} = 14.7$  Hz), 7.41 (Ar, s, 10H);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 12.4 (Me, d,  $J_{\text{PC}} = 87.4$ ), 120.9 (d,  $J_{\text{PC}} = 4.4$  Hz), 127.9 (d,  $J_{\text{PC}} = 1.6$  Hz), 131.2 (d,  $J_{\text{PC}} = 1.1$  Hz), 149.3 (d,  $J_{\text{POC}} = 11.0$  Hz) (Ar);  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 96.6 (septet). Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{BrO}_2\text{P}$ : C, 51.4; H, 4.9. Found: C, 50.3, H, 4.9.

**Thermal disproportionation of dimethyldiphenoxyphosphonium bromide (5a).** (a) A sample of the recrystallized bromide **5a** (*ca.* 0.2 g) was heated until it melted (210 °C) and then for a further 7.5 days, to give a mixture containing  $(\text{PhO})_2\text{PMe}_2\text{Br}$  (36.5 mole%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.89 (Me, d,  $^2J_{\text{PCH}} = 15.0$  Hz),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 96.0 (septet);  $\text{PhOPMe}_3\text{Br}$  (35.3 mole%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.59 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 102.2 (decet);  $(\text{PhO})_2\text{P(O)Me}$  (28.2 mole%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.75 (Me, d,  $^2J_{\text{PCH}} = 17.8$  Hz),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 23.9 (quartet);  $(\text{PhO})_3\text{P}$  (trace),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 125.1. In a similar experiment at 210 °C (12 days), the following additional products were detected:  $\text{PhOP(O)Me}_2$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.70 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz);  $\text{Me}_3\text{PO}$ ,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.19 (Me, d,  $^2J_{\text{PCH}} = 14.0$  Hz).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.70 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz).

(b) In a further experiment, with a gradual increase in temperature during 46 h from 190-290 °C, the product contained  $\text{PhOPMe}_3\text{Br}$  (24.0 mole%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 2.53 (Me, d,  $^2J_{\text{PCH}} = 14.0$  Hz),  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ) 101.9 (m);  $(\text{PhO})_2\text{P(O)Me}$  (48.5 mole%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.74 (Me, d,  $^2J_{\text{PCH}} = 17.7$  Hz),  $\delta_{\text{P}}$

(CDCl<sub>3</sub>) 23.9 (quartet); PhOP(O)Me<sub>2</sub> (14.9 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.78 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 60.3; Me<sub>4</sub>PBr (12.5 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.12 (Me, d,  $^2J_{\text{PCH}} = 14.7$  Hz);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 22.6. (PhO)<sub>3</sub>PO,  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) -17.7 was also detected.

**Isolation of dimethyldiphenoxyphosphonium iodide (5b).** Methyltriphenoxyphosphonium iodide **4b** (16.0 g, 35.4 mmol) was heated alone (molten) in a sealed glass tube (175 °C) for 120 h. After cooling and the removal of volatiles (iodobenzene,  $\delta_{\text{H}}$  6.7-7.9, plus some methyl iodide,  $\delta_{\text{H}}$  2.12) under reduced pressure, the dark viscous residue contained (PhO)<sub>2</sub>P(O)Me (47.8 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.73 (Me, d,  $^2J_{\text{PCH}} = 17.7$  Hz); (PhO)<sub>2</sub>PMe<sub>2</sub>I (18.4 mole%)  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.64 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz); (PhO)<sub>3</sub>PMeI (33.8 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.83 (Me, d,  $^2J_{\text{PCH}} = 16.8$  Hz); and a trace of a compound,  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.12 (Me, dd), containing the structure MeP-O-P (see also below). The addition of anhydrous ether gave a solid product which was recrystallized several times from acetone and ether, then from acetonitrile and ether, and finally dried in *vacuo* to give dimethyldiphenoxyphosphonium iodide **5b** (1.0 g, 2.67 mmol), m.p. 152-155 °C (sealed tube),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.91 (Me, d, 6H,  $^2J_{\text{PCH}} = 14.4$  Hz), 7.45 (Ar, s, 10H);  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 13.2 (Me, d,  $J_{\text{PC}} = 87.9$ ), 120.5 (d,  $J_{\text{PC}} = 4.3$  Hz), 121.2 (s), 128.0 (s), 131.3 (s), 149.1 (d,  $J_{\text{POC}} = 11.0$  Hz) (Ar);  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 94.8 (septet). Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>IO<sub>2</sub>P: C, 44.9; H, 4.3; I, 33.9. Found: C, 43.3, H, 4.3; I, 33.9.

**Thermal disproportionation of dimethyldiphenoxyphosphonium iodide (5b).** A sample of the recrystallized iodide **5b** (*ca.* 0.2 g) was heated (molten) in a sealed glass tube (190-240 °C) for 28.5 days to give a mixture containing (PhO)<sub>2</sub>PMe<sub>2</sub>I (26.0 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.80 (Me, d,  $^2J_{\text{PCH}} = 14.4$  Hz),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 93.7 (m); PhOPMe<sub>3</sub>I (36.2 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.60 (Me, d,  $^2J_{\text{PCH}} = 13.8$  Hz),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 100.4 (m); (PhO)<sub>2</sub>P(O)Me (37.8 mole%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.75 (Me, d,  $^2J_{\text{PCH}} = 17.8$  Hz); (PhO)<sub>3</sub>PMeI (trace),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 40.4.

**Thermal decomposition of methyltriaryloxyphosphonium halides in CDCl<sub>3</sub>.** Solutions containing 8 or 10% w/v of each of the methyltriaryloxyphosphonium halides (**4a**, **4b**, **13a**, **13b**) in CDCl<sub>3</sub> were heated in sealed NMR tubes as specified and the products were analyzed by a combination of <sup>1</sup>H and <sup>31</sup>P NMR. Results for the bromides (**4a**, **13a**) are shown in Tables 3 and 4 and for the iodides (**4b**, **13b**) in Tables 5 and 6.

**Formation of *o*-bromotoluene in the thermal decomposition of methyltri-*o*-tolylxyphosphonium bromide (13a).** The bromide **13a** (3.0 g) was heated (2 h at 200 °C) in a distillation apparatus at 0.1 mmHg. A cold trap (-80 °C) collected a clear liquid (< 0.5 g) consisting of *o*-bromotoluene (80%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.35 (s) and *o*-cresol (20%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.20 (s). Further heating (3 h at 200 °C) gave a liquid distillate (1.8 g), b.p. 160-180 °C at 0.05-0.1 mmHg, containing di-*o*-tolyl methanephosphonate **14** (52.4%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 1.78 (MeP, d,  $^2J_{\text{PCH}} = 17.4$  Hz), 2.21 (*o*-Me, s),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 23.9 (quartet), *o*-bromotoluene (18.2%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.34 (s), and *o*-cresol (29.4%),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.17 (s). GLC analysis of both distillates on 10% PEGA at 115 °C (see above) confirmed the identities of *o*-cresol (*t<sub>R</sub>* 5 min 35 sec) and of *o*-bromotoluene (*t<sub>R</sub>* 38 min 50 sec). *m*-Bromotoluene (*t<sub>R</sub>* 42 min 10 sec) was not detectable.

**Isolation of P-O-P intermediate from the products of thermal decomposition of methyltri-*o*-tolylxyphosphonium bromide (13a).** The dark brown residue from the above experiment

(0.5 g) was dissolved in chloroform and treated with anhydrous ether to give an oily mass containing white crystals. The latter were separated by decantation, washed with dry ether, dried *in vacuo*, and immediately analyzed by NMR which indicated the intermediate **23** (Ar = *o*-tolyl):  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 2.02 (9H, *o*-MeC<sub>6</sub>H<sub>4</sub>, d,  $^5J_{\text{POCCCH}}$  0.9 Hz), 2.18 (6H, *o*-MeC<sub>6</sub>H<sub>4</sub>, d,  $^5J_{\text{POCCCH}}$  0.9 Hz), 2.38 (3H, Me-P-O-P, dd,  $^2J_{\text{PCH}}$  13.9 Hz,  $^4J_{\text{POPCH}}$  1.9 Hz), 7.20 (20H, Ar, br s),  $\delta_{\text{P}}$  (CDCl<sub>3</sub>) 32.3 (Me-P-O-P,  $J_{\text{POP}}$  32.4 Hz), 77.0 (Me-P-O-P, dq,  $J_{\text{POP}}$  32.4 Hz,  $J_{\text{PCH}}$  16.0 Hz). Instability on storage precluded further examination.

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13. The formation of *o*-bromotoluene (**15**, X = Br), with none of the corresponding *m*-isomer, confirms the view that benzyne intermediates are not involved in this type of reaction and that bimolecular nucleophilic displacement most probably occurs (*cf.* ref. 11, p.389). The observation in the present work of the development of a deep blue coloration, considered to be indicative of the presence of phenyl radicals (*cf.* Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin: California Reading, Mass. 2<sup>nd</sup> Edition, 1981, p 1302) during the thermolysis of **13a** in CDCl<sub>3</sub> at 150 °C, is interesting. However, the extent to which free radicals might be involved in the Michaelis-Arbuzov reaction under these conditions has not been established.
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16. Catalysis of the Michaelis-Arbuzov reaction by phosphonate was recognized many years ago (*cf.* R. G. Harvey and E. R. De Sombre in ref. 1, p. 76) but the mechanism of catalysis was uncertain. The examples reported were reactions of trialkyl phosphites, for which intermediates had not at that stage been clearly identified.
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