# Phosphinic Acids and Derivatives. Pyrolytic Elimination in Phosphinate Esters[1]

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Abstract: The pyrolytic elimination reaction of esters of diphenylphosphinic acid, $(C_6H_5)_2PO_2H$, has been studied with regard to scope, conditions, products, rates, and mechanism. Tertiary esters eliminate very readily at $\sim100°$, but the reaction also takes place with secondary and primary esters at $\sim300°$. Rearranged products are frequently observed, but not in the ratios expected from carbonium ions. Elimination is catalyzed by added acid and the rate law is $v = k[\text{ester}][\text{acid}]$. Relative rates at $126°$ were determined for the following esters: isobutyl (1), n-propyl (2), neopentyl (3), isopropyl (3×10^2), pinacolyl (4×10^2), and tert-butyl (2×10^6). On the basis of these results, it is concluded that a mechanism with ion-pair character (carbonium cation–phosphinate anion) is involved.

Amine oxides (1) eliminate readily[3] by a cyclic mechanism; this is probably the best example of this mechanism of elimination.[4] Carboxylate esters (2) require considerably higher temperatures for pyrolytic elimination and the cyclic mechanism may not be as generally valid, considering all cases, as in amine oxides.[4,5] Although the P=O group in 3 is not as basic[6] or as polar as the NO group in N-oxides (1),[7,8] it is considerably more basic than the carbonyl of carboxylates (2).[9] Because of this factor and the greater ease of breaking the C–O bond in 3 than the C–N bond in 1, phosphorus esters represent an interesting example in elimination reactions. We have, therefore, investigated the pyrolytic elimination of diphenylphosphinate esters (4) in considerable detail.
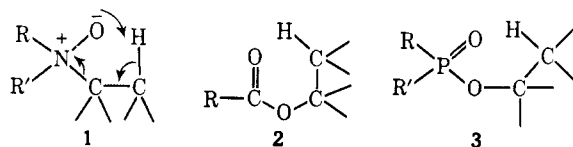
Pyrolytic elimination reactions have been noted in phosphate esters (6). Baumgarten and Setterquist[10] reported the formation of olefins from mixed trialkyl phosphates, but the composition of the olefins was not quantitatively determined. In the pyrolysis of n-butyl phosphates,[11] 1-butene, cis-2-butene, and trans-2-butene were obtained as products. Acid catalysis was observed. A small amount of rearrangement of starting material was not sufficient to account for the amount of 2-butene in the products. A study by Hanneman and Porter[12] on dialkyl phosphates (6, R'' = H) also included a demonstration of acid-catalyzed decomposition. The olefinic products were identified and approached a mixture close to that which would be expected if the olefins were generated from the thermodynamically most stable carbonium ion. The evidence from these studies of phosphates therefore points to an ionic carbonium ion mechanism for pyrolytic decompositions. During the course of this research, reports appeared on the synthesis[13] and pyrolysis[14] of alkyl esters of diphenylphosphinic acid (4). Although there was some difficulty in explaining the large percentages of 2-octenes from the pyrolysis of 2-octyl diphenylphosphinate, the mechanism thought to be most consistent with their data was a cyclic cis elimination.

Results

Product Studies. During the determination of the melting point of tert-butyl diphenylphosphinate (4, R = tert-butyl), this ester melted sharply at 108–109°, but at approximately 115° evolution of gas was observed. A white crystalline solid was deposited on the walls of the capillary tube, and upon further heating this solid melted at 194–195°. The gas produced in this decomposition was trapped with the aid of a high vacuum system. A mass spectrum of the gas was consistent with the structure of isobutene.[15] The white crystalline residue after evolution of gas was shown to be diphenylphosphinic acid (5).

Similar experiments were performed on other esters. Where mixtures of olefins were possible, the composition of the pyrolysate was determined by glc. The results are given in Table I together with the calculated percentages based on thermodynamic stabilities.[16] In

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(14) K. D. Berlin and T. H. Austin, *ibid.,* 30, 2745 (1965).

(15) Catalog of Mass Spectral Data, American Petroleum Institute Research Project No. 44, Carnegie Institute of Technology, Pittsburgh, Pa.

(16) J. E. Kirkpatrick, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Nat. Bur. Stand.,* 36, 559 (1946).

Table I. Pyrolysis Conditions and Olefin Compositions from Alkyl Diphenylphosphinates, $(C_6H_5)_2P(O)OR$

Ester	Conditions	Yield, %	Olefins	Obsd, %[d]	Calcd, %[d,e]
tert-Butyl	120°, 15 min		Isobutene		
Isopropyl	270°, 15 min		Propene		
Isobutyl	335°, 15 min		Isobutene	95	50.4
			trans-2-Butene	3.0	31.2
			cis-2-Butene	2.0	18.4
Pinacolyl[a]	300°, 1 min	97	3,3-Dimethyl-1-butene	18	3.3
			2,3-Dimethyl-1-butene	52	41.6
			2,3-Dimethyl-2-butene	31	54.6
Neopentyl[b]	360°, 5 min	96	2-Methyl-2-butene	56	65.2
			2-Methyl-1-butene	44	34.8
Menthyl[c]	290°, 5 min	92	3-Menthene	56	
			2-Menthene	44	

[a] Five olefinic products were detected by glc. Two were present in very low amounts (0.5% of total) and were not identified. The per cents shown are the average of two runs. [b] Averages of three runs and four determinations are shown. [c] Yield and per cent are shown for only one run. In two other runs, yield was about 50%, but compositions were similar to the run shown (57, 56% and 43, 44%). The glc analysis also revealed five small peaks which were about 4% of the total pyrolysate. These were not identified. [d] Composition in mole %. [e] Calculated for a mixture at equilibrium in the gas phase; ref 16.

the case of the pinacolyl, neopentyl, and 1-menthyl esters, the decomposition is complete in 5 min or less. The olefins which resulted from the pyrolysis of these three esters were subjected to control experiments in a closed system in the presence of **5** at the temperatures
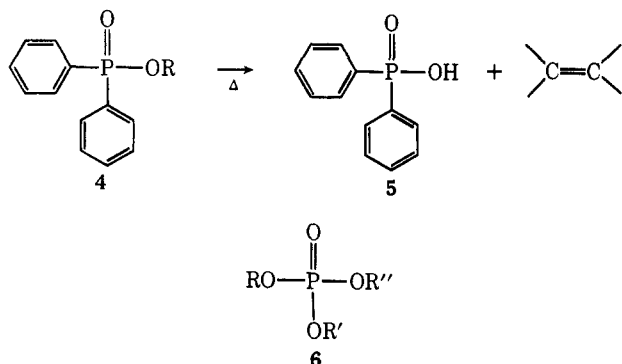

and reaction times which were employed for the pyrolyses. Within experimental error, *no isomerization* of the olefins *was observed*. The fact that no isomerization of these olefins took place may be due to the very short reaction times.[17]

Rate Studies.[18] O'Connor and Nace[19] have reported the kinetics of decomposition of various alkyl xanthates in the liquid phase at temperatures from 146 to 206° using the loss in weight due to evolution of olefin as the analytical method. This method was applicable to the pyrolysis of diphenylphosphinates. When the pyrolysis of the isopropyl ester (**4**, R = $CH(CH_3)_2$) in the liquid phase was conducted at 241°, the data did not obey first-order kinetics. A plot of per cent reaction *vs.* time produced an S-shaped curve (Figure 1, curve at

(17) Berlin and Austin[14] also carried out control experiments but at the boiling points of 1-octene and *cis*-2-octene, whereas their pyrolyses were carried out at much higher temperatures.

(18) Several methods were tested for suitability for kinetic measurements. Since an acid (**5**) is a product, titration was first employed as the analytical method. The solvent had to have a high boiling point, be thermally stable, and be an adequate solvent for **4** and **5**. Therefore, the elimination of isopropyl diphenylphosphinate was attempted in diethylcarbitol (bp 188°) at 151° under a purified nitrogen atmosphere. Even after 74 hr at this temperature, titrations indicated a negligible amount of reaction (approximately 2%), and the solvent appeared to be decomposing since a yellow color had formed in the solution. In fact, the figure of 2% reaction may have been due to the formation of acidic decomposition products from solvent. Experiments in dimethyl sulfoxide were also unsuccessful due to solvent decomposition.

(19) G. L. O'Connor and H. R. Nace, *J. Amer. Chem. Soc.*, **74**, 5454 (1952).

right) indicative of a reaction which follows second-order autocatalytic kinetics.[20]

In order to determine the possibility of acid catalysis for the reaction, isopropyl diphenylphosphinate was pyrolyzed with differing amounts of diphenylphosphinic acid. Figure 1 shows the results of these pyrolyses in a plot of per cent reaction *vs.* time. The approximate times of pyrolysis for 50% reaction are 49, 11, and 7.5 min for 1.2, 25, and 50 mole % of the added diphenylphosphinic acid, respectively. Similar evidence for acid catalysis was obtained in the pyrolysis of the *n*-propyl and isobutyl esters. For example, 50% reaction is reached at 825 min without acid and 310 min with 25 mole % acid in the case of *n*-propyl ester at 226°. For the isobutyl ester at 226°, 50% reaction is reached at 390 min without acid and 107 min with 25 mole % acid. These experiments demonstrate that *the thermal decomposition of alkyl diphenylphosphinates is acid catalyzed*.

Equation 1 gives the stoichiometry for this second-order, autocatalytic reaction. If E_0 and A_0 are the initial concentrations of ester and acid, one obtains the

$$A + E \xrightarrow[\Delta]{k} 2A + \text{olefin} \qquad (1)$$
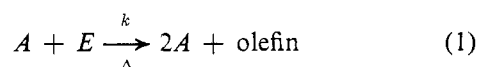
integrated rate equation 2 which can be rearranged to 3. A plot of log (A/E) (obtained from measurements of weight loss) *vs.* time yields a straight line with a slope,

$$\frac{1}{E_0 + A_0} \ln (E_0 A / A_0 E) = kt \qquad (2)$$

$$\log (A/E) = (E_0 + A_0)kt/2.3 + \log (A_0/E_0) \qquad (3)$$

$m = (E_0 + A_0)k/2.3$. However, E_0 and A_0 are inaccurately known because of the unknown density of the melt at the reaction temperature. We therefore arbitrarily set $(E_0 + A_0) = 2.3 M$. Since the melt composition changes during reaction, the absolute values of k are not very accurate and this assumption, therefore, seems adequate. We are most concerned with relative rates. In order to minimize errors in relative rates, the ratio of E_0 to A_0 was constant in the determinations used for estimation of relative rates.

(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, Wiley, New York, N. Y., 1961, p 19.
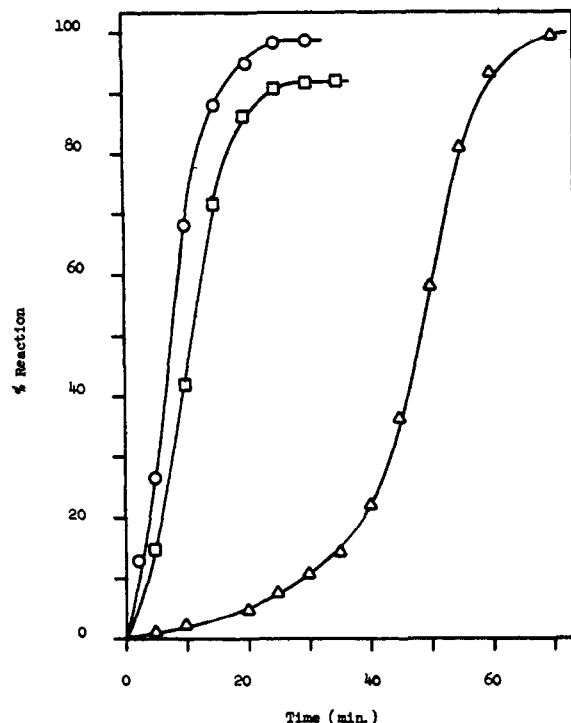
Figure 1. Per cent reaction *vs.* time for the pyrolysis of isopropyl diphenylphosphinate as a function of $[(C_6H_5)_2PO_2H]$; $\triangle$, 1.2 mole % acid; $\square$, 25 mole % acid; $\bigcirc$, 50 mole % acid.

Figure 2. Plot of log (A/E) *vs.* time for pyrolysis of isopropyl diphenylphosphinate at 210°.

The isopropyl, *n*-propyl, isobutyl, pinacolyl, and neopentyl esters were pyrolyzed at temperatures ranging from 200 to 241° keeping $(E_0/A_0) = 3$. Hydroquinone was added to some pyrolysis mixtures (4–11 mg) in order to suppress any free radical reactions which might be initiated by atmospheric oxygen. Figure 2 shows data for the isopropyl ester plotted as log (A/E) *vs.* time. A reasonable straight line is obtained from Figure 2 with slope, $m = 2.6 \times 10^{-2}$ min^{-1}. Similar plots were obtained with the *n*-propyl, isobutyl, pinacolyl, and neopentyl esters and the data are summarized in Table II.[21]

Considerable difficulties were encountered in the attempted pyrolysis of the *tert*-butyl ester. The *tert*-butyl ester has an inconveniently rapid pyrolysis rate only slightly above its melting point (109°). After the reaction begins, the liquid melt soon turns to a solid due to formation of diphenylphosphinic acid (mp 194°). The pyrolysis temperature cannot be raised above the melting point of diphenylphosphinic acid because the rate would then be too fast to measure. The *tert*-butyl ester was, therefore, pyrolyzed at a temperature of 126° without added diphenylphosphinic acid and with 1 mole % of the acid. In both cases, it was possible to take one measurement before the melt solidified. The pyrolysis of the *tert*-butyl ester without added acid was 64.8% completed after 5 min; in the mixture containing 1 mole % acid, the reaction was 66.6% completed after 5 min. The *k* for the *tert*-butyl ester in Table II is based

on this measurement and the assumption of the rate law in eq 3.

A comparison of relative *k* values is shown in Table III. In order to compare the *tert*-butyl ester with the other esters, we extrapolated for the neopentyl, *n*-propyl, isobutyl, isopropyl, and pinacolyl esters to 126°, the temperature at which a direct estimate of the rate of pyrolysis of the *tert*-butyl ester was made from the above data. The comparison at 210.4° is based on direct measurements except for the *n*-propyl ester. These data reveal orders of magnitude for the relative rates of pyrolysis of these esters. Based on the values for 126°, the reactivity order for the pyrolysis of these esters is: tertiary > secondary > primary in the approximate ratio $10^6:10^2:1$.

Partial Pyrolysis of the Pinacolyl Ester. A sample of pinacolyl diphenylphosphinate was pyrolyzed at 226° to 39% reaction in order to determine if rearrangement could be observed in the pyrolysis of the diphenylphosphinates. Analysis of the resulting mixture of diphenylphosphinic acid and ester by nmr showed that no detectable rearrangement of the pinacolyl ester (to the 2,3-dimethyl-2-butyl ester) had taken place.[22]

Discussion

Phosphinate esters are easily synthesized from alcohols (see Experimental Section). These results demonstrate that alkyl phosphinates eliminate quite readily. Considerably lower temperatures are required than were necessary for the pyrolytic elimination of dialkyl oxalates.[23] However, the products are mixed and the reaction appears to be less clean and requires considerably higher temperatures than elimination reactions of amine oxides.[4]

Mechanism. Three mechanisms appear possible for the pyrolytic elimination of alkyl diphenylphosphinates: (1) a free radical mechanism; (2) a carbonium ion mechanism; (3) a cyclic, cis-elimination mechanism. Results obtained in this work indicate that a free radical mechanism is unlikely because the addition of hydroquinone has no effect on the rate of pyrolysis (Table II). If the reaction were proceeding by way of free radicals, one would expect considerable rate retardation in the

(21) Most, but not all of the kinetic plots gave good straight lines. In the pyrolysis of the isopropyl ester at 226°, curvature appeared after 25 min (92% reaction). This curvature is most likely due to small amounts of ester distilling into the cold part of the pyrolysis tube and thus escaping decomposition. This source of error shows up in a plot of log (A/E) *vs.* time as a downward curvature toward the end of the reaction.
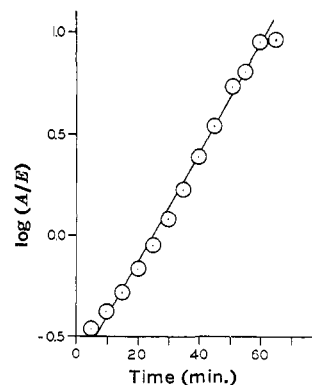
(22) This result is not entirely unexpected since the resulting rearranged tertiary ester, if produced, would be expected to decompose much faster than the secondary ester and thus escape detection.

(23) G. J. Karabatsos and K. J. Krumel, *J. Amer. Chem. Soc.*, **91**, 3324 (1969).

Table II. Rate Data for Pyrolysis of Alkyl Diphenylphosphinates

Ester	T, °C^a	$E_0{}^b$	$A_0{}^b$	HQ^c	% R^d	10^3k, M^{-1} min^{-1} ^{e}
Isopropyl	225.9	2.62	0.03	4.4	0–97	54.7 ± 1.2
	225.9	3.45	3.46		13–99	81.2 ± 4.4
	225.9	3.12	1.03		15–86	80.6 ± 2.6
	225.9	2.12	1.03	5.4		79.1 ± 6.2
	210.4	3.12	1.03	8.1	1–87	26.0 ± 0.7
	199.9	3.12	1.03	4.9	2–89	16.3 ± 0.5
n-Propyl	225.9	3.28				1.91 ± 0.73
	225.9	3.12	1.03			2.12 ± 0.06
	225.9	3.12	1.03	6.2	4–94	2.80 ± 0.10
	243.1	3.12	1.03	5.6	5–88	7.78 ± 0.30
	199.9	3.12	1.03	5.6	1–9	0.37 ± 0.02
Isobutyl	225.9	2.86			0–95	8.43 ± 0.36
	225.9	3.12	1.03		18–83	10.8 ± 0.9
	225.9	3.12	1.03	5.2	32–98	11.8 ± 0.2
	210.4	3.12	1.03	5.2	1–25	2.00 ± 0.07
	241.1	3.12	1.03	6.6	12–97	32.2 ± 3.6
	241.1	3.12	1.03	10.9	14–85	19.4 ± 0.4
Pinacolyl	225.9	1.89			2–9	53.5 ± 5.0
	225.9	2.15			1–40	62.4 ± 3.7
	225.9	1.76			1–15	54.6 ± 0.8
	210.4	3.12	1.03	5.4	3–98	56.6 ± 2.2
	199.9	3.12	1.03	6.2	14–80	29.7 ± 1.0
Neopentyl	225.9	3.12	1.03	6.0	2–29	0.88 ± 0.06
	210.4	3.12	1.03	7.0	4–20	0.34 ± 0.01
$tert$-Butyl^f	126	3	1		0–67	0.2

^{a} Error in T is less than ±0.2. ^{b} E_0 and A_0 are initial quantities of ester and acid, respectively, given in millimoles. ^{c} Weight of hydroquinone in milligrams. ^{d} Per cent reaction over which data were obtained. ^{e} The k values were determined from the slope m of a plot of log (A/E) $vs.$ time by setting $(E_0 + A_0) = 2.3$ M in which case $k = m;$ error is the standard deviation (W. J. Youden, "Statistical Methods for Chemistry," Wiley, New York, N. Y., 1951). ^{f} Both temperature and k are inaccurate for the $tert$-butyl ester since k was determined from one point: 66.6% reaction in 5 min. This value was used to solve eq 3 for k.

Table III. Relative Rates of Pyrolysis of Alkyl Diphenylphosphinates^a

Ester	$k_{\text{relative}}{}^{210.4°}$	$k_{\text{relative}}{}^{126°}$
Neopentyl	1.0	3
n-Propyl	2.4	2
Isobutyl	6.0	1
Isopropyl	78	3 × 10^2
Pinacolyl	170	4 × 10^2
$tert$-Butyl		2 × 10^6

^{a} In order to obtain values at temperatures other than those where k was directly measured, plots of log k $vs.$ $1/T$ were constructed for each of the esters listed in Table II.

presence of hydroquinone. This is consistent with Berlin and Austin's results.[14]

Product Studies. The product studies show that pyrolysis of alkyl diphenylphosphinates results in some rearranged olefins. The formation of olefins appears to be a kinetically controlled process, because the observed olefin compositions (Table I) do not closely resemble the equilibrium olefin composition.[16]

These results are not explicable by an E_i (cyclic) mechanism. The pyrolysis of pinacolyl diphenylphosphinate via an E_i mechanism would have produced only 3,3-dimethyl-2-butene. However, the rearranged olefins 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene were produced in larger amounts than 3,3-dimethyl-1-butene. This strongly indicates that the reaction is taking place through a mechanism with carbonium ion character, since the dehydration of pinacolyl alcohol, which is thought to proceed by an E_1 mechanism, gives 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene in the ratio of 5 to 2.[24] The formation of cis- and $trans$-2-butene in the pyrolysis of isobutyl diphenylphos-

phinate gives strong support to this conclusion since an E_i mechanism could give only the terminal olefins. The pyrolysis of neopentyl diphenylphosphinate gives a mixture of 2-methyl-2-butene and 2-methyl-1-butene as expected if there is a mechanism with carbonium ion character as in the gas-phase pyrolysis of neopentyl chloride.[25]

Rate Studies. The rate data show that the pyrolysis of the phosphinates is an acid-catalyzed reaction. The acid catalysis, the second-order autocatalytic kinetics, and the relative rates can best be explained on the basis of a carbonium ion mechanism. The fact that authentic E_i (cyclic) pyrolyses obey first-order kinetics and do not seem to be acid catalyzed indicates an E_i mechanism is improbable here.

It is interesting to compare the relative rates of pyrolysis of diphenylphosphinates with the pyrolysis of acetates, chlorides, and amine oxides (Table IV). The relative rates of pyrolysis of the acetates, chlorides, and phosphinates qualitatively parallel one another, but are quite different from the relative rates of the amine oxides.[4,26] The relative rates of the acetates, chlorides, and phosphinates are all very dependent on the degree of branching at the α-carbon atom, indicating that the transition state has some carbonium ion character.[27] The relative rate ratio of $1:10^2:10^6$ for the reactivity of primary, secondary, and tertiary alkyl diphenylphosphinates is similar to the relative rates of S$_N$1 reactions. In formic acid at 100°, the relative rates of S$_N$1 reactions of ethyl, isopropyl, and $tert$-butyl bromide are reported to be in the ratio $1:26:10^8$.[28] This sug-

(24) F. C. Whitmore and H. S. Rothrock, $J.$ $Amer.$ $Chem.$ $Soc.$, 55, 1106 (1933).

(25) A. Maccoll and E. S. Swinburne, $Proc.$ $Chem.$ $Soc.$, 409 (1960).
(26) A. C. Cope, N. A. Lebel, H. H. Lee, and W. R. Moore, $J.$ $Amer.$ $Chem.$ $Soc.$, 79, 4720 (1957).
(27) A. Maccoll in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 203.

Table IV. Relative Rates of Pyrolysis of Amine Oxides, Acetates, Chlorides, and Diphenylphosphinates

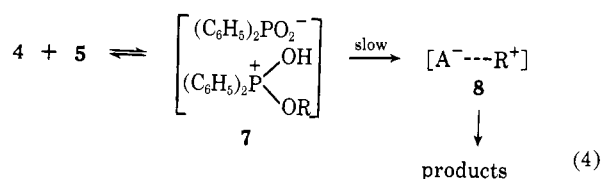| Alkyl group	Amine oxide at 100° [a]	Acetate at 100° [b]	Chloride at 100°	Phosphinate at 126° [c]
Ethyl	1.00	1.0	1.0	
n-Propyl	0.60		1.7×10^1	2
Isopropyl	2.64	6.4×10^1	6.8×10^4	8×10
tert-Butyl	6.06	8.1×10^4	1.5×10^9	2×10^6

[a] Approximate temperature; data from ref 26. [b] Relative rates extrapolated from data at higher temperatures; data from ref 27. [c] Neopentyl ester is taken as 1 for relative rate comparison; see Table II.

Table V. Yields, Melting and Boiling Points, and Carbon–Hydrogen Analysis of Alkyl Diphenylphosphinates, $(C_6H_5)_2P(O)OR$

R	Method of prep	Yield, %	Bp (mm) or mp, °C[d]	Anal., %[g] Carbon Calcd	Found	Hydrogen Calcd	Found
Methyl	B	98	159 (1.1)[e]	67.24	67.38	5.64	5.55
Ethyl[h]	B	100	150–151 (0.1)[f]	65.87	65.89	6.32	6.15
Isopropyl[a]	B	93	100.6–101.5[e]	69.22	69.35	6.58	6.68
n-Propyl[b]	A	83	90.7–92.7	69.22	69.48	6.58	6.86
Isobutyl[a]	A	81	80.8–82.8	70.06	70.13	6.98	6.98
tert-Butyl[a]	B	56	108.6–109.6[e]	70.06	70.22	6.98	7.01
Neopentyl[b]	A	96	86.2–86.7	70.82	70.95	7.34	7.46
Pinacolyl[c]	B	42	63.0–64.0	71.51	71.67	7.67	7.68
1-Menthyl	A	88	71.3–72.3	74.13	74.27	8.18	8.02

[a] Recrystallized from acetone. [b] Recrystallized from hexane–acetone. [c] Recrystallized from pentane. [d] Melting points were taken on a Mel-Temp block and are corrected. [e] Reported boiling and melting points in ref 13: methyl, 178° (2.4 mm); isopropyl, 97–99°; and tert-butyl, 111–112°. [f] Lit. bp 173–175° (1.5 mm); G. M. Kosolapoff and W. F. Huber, *J. Amer. Chem. Soc.*, **69**, 2020 (1947). [g] Carbon–hydrogen analyses were performed by Miss Heather King, Department of Chemistry, University of California at Los Angeles. [h] Theoretical carbon–hydrogen values were calculated for the hydrated ethyl ester having the formula $C_{14}H_{15}PO_2 \cdot 0.5H_2O$. This composition was deduced also from the nmr spectrum.

gests that the pyrolytic elimination of alky diphenylphosphinates may be characterized by decomposition of the protonated ester (4-H⁺) through a transition state with considerable carbonium ion character (eq 4). The structure of the ion pairs **7** and **8** might be expected to have considerable influence on the distribution of products since the anions would be expected to be the base functioning in proton removal from free or partially associated R⁺. The degree of association in **8** will ob-

$$4 + 5 \; \rightleftharpoons \; \begin{bmatrix} (C_6H_5)_2PO_2^- \\ \quad \overset{+}{\diagup} OH \\ (C_6H_5)_2P \diagdown \\ \quad\quad OR \end{bmatrix} \xrightarrow{slow} [A^- \text{---} R^+] \atop \mathbf{8}$$

$$\mathbf{7}$$

$$\downarrow$$

$$products \quad\quad (4)$$

viously depend on the stability of R⁺; primary carbonium ions are not likely to be free. The A⁻ ion is probably a dimer monoanion, $[(C_6H_5)_2PO_2HO_2P(C_6H_5)_2]^-$, which offers several basic sites and may account for the unique distribution of products we have observed in this reaction.

A carbonium ion mechanism for the pyrolysis of alkyl diphenylphosphinates was rejected by Berlin and Austin[14] on the basis that the pyrolysis of n-octyl diphenylphosphinate gave only 4% 2-octene. These workers felt that a carbonium ion mechanism would have given more isomeric octenes than observed and, therefore, favored a cyclic, E_i mechanism. This obviously depends upon the lifetime and state of association of the carbonium ion. The pyrolysis of diphenylphosphinates, under the conditions of Berlin and Austin and also under the conditions used in this study, is undoubtedly kinetically controlled. It is quite pos-

sible that an ion-pair mechanism would only give rise to 4% 2-octene since rearrangement requires a hydride shift, and this rearrangement may not compete favorably with abstraction of a proton to give 1-octene. The pyrolysis of 2-octyl diphenylphosphinates yields 21% 1-octene, 21% cis-2-octene, and 58% trans-2-octene.[14] The predominance of trans-2-octene over cis-2-octene was explained[14] by postulating conformational preferences. However, there was difficulty in rationalizing the overall predominance of 2-octene over 1-octene, since the predicted distribution of products for an E_i mechanism would be 60% 1-octene and 40% 2-octene.[4] If one assumes an ion-pair intermediate **8** for this pyrolysis, there is no difficulty in rationalizing the predominance of 2-octene over 1-octene; elimination from a carbonium ion generally gives the Saytzeff product, and therefore 2-octene would be expected to predominate over 1-octene.

Of course, in some esters there may be merging between mechanisms and the ethyl ester may have some E_i character in its elimination reaction. But the general character of this reaction is given in eq 4.

Experimental Section

Technical grade diphenylphosphinous chloride was obtained from Victor Chemical Co. and was used without further purification. Methyl, ethyl, and isopropyl alcohol were purified according to methods described by Vogel.[29] Benzene was used without further purification, but was dried and stored over sodium wire or sodium-lead alloy. Dimethyl sulfoxide was purified by distillation from calcium hydride. Diethylcarbitol was purified by distillation from sodium. tert-Butyl alcohol was dried over anhydrous potassium carbonate and then distilled. Used without further purification were 1-menthol from Eastman, pinacolyl alcohol from Columbia Organic Chemicals Company, neopentyl alcohol from Aldrich Chemical Company, and pyridine, 1-propanol, 2-butanol, alum-

(28) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 43. The rate for ethyl bromide may, of course, have a considerable S_N2 component.

(29) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green, and Co., New York, N. Y., 1956.

Table VI. Infrared Spectral Data for Alkyl Diphenylphosphinates[a]

Alkyl group	P-phenyl	P=O	P-O-C	Solvent
Methyl	1437	1230	1030	CCl₄
Ethyl	1439	1228	1033	CHCl₃
Isopropyl	1444	1222	982	CHCl₃
tert-Butyl	1437	1229	978	CCl₄
n-Propyl	1437	1228	981	CCl₄
Isobutyl	1437	1210	1012	CHCl₃
Neopentyl	1437	1209	1010	CHCl₃
Pinacolyl	1433	1203	956	CHCl₃
1-Menthyl	1437	1225	982	CCl₄

[a] Wavelengths are given in cm⁻¹; infrared spectra were taken in the liquid phase on a Perkin-Elmer Model 421 infrared spectrophotometer.

in 100 ml of dry CH_3OH was slowly added with stirring. Sodium chloride was removed by filtration, and the filtrate was washed with two 50-ml aliquots of cold 5% Na_2CO_3 and three 50-ml aliquots of H_2O. The benzene phase was dried over anhydrous $MgSO_4$ and then evaporated to a residual oil which was vacuum distilled through a 25-cm tantalum wire column equipped with heated jacket, bp 232° (2.9 mm). Methyl diphenylphosphinate crystallized upon standing at room temperature (41.1 g, 97.7% of theory).

Characterization. Handling the esters was straightforward except for the methyl ester which is slightly hygroscopic and the ethyl ester which is extremely hygroscopic. When the ethyl ester was exposed to atmospheric moisture and allowed to come to constant weight before combustion analysis, the carbon–hydrogen analysis and nmr spectrum agreed with the formula $C_{14}H_{15}PO_2 \cdot 0.5H_2O$. The structures of all esters were in agreement with carbon–hydrogen analyses and nmr and infrared spectroscopy (Tables V–VII).

Table VII. Chemical Shifts and Coupling Constants in Alkyl Diphenylphosphinates, $(C_6H_5)_2PO_2-C_1-C_2-C_3$[a]
$$| \quad C_4$$

Ester	C₁	C₂	C₃	C₄
Methyl[b]	6.41, d, 11.0			
Ethyl[b]	6.03, p, 7.5	8.70, t, 7.5		
Isopropyl[c]	5.3, m	8.68, d, 6.0		
tert-Butyl[b]		8.53, s		
n-Propyl[c]	6.10, q, 6.5	8.37, x, 7	9.05, t, 7.0	
Isobutyl[c]	6.22, t, 6.5	8.0, m	9.07, d, 6.5	
Neopentyl[c]	6.33, d, 5.0		9.03, s	
Pinacolyl[c]	5.7, m		9.07, s	8.78, d, 6.5
1-Menthyl[b]	5.5–6.2, m	Remaining H's are a multiplet at τ 7.55–9.67		

[a] All chemical shifts are in $\tau = 10 - \delta$, $(CH_3)_4Si$ as internal standard. Coupling constants are in hertz. Splitting symbols are: s = singlet, d = doublet, t = triplet, q = quartet, p = pentuplet, x = sextet, m = multiplet. In all cases, the phenyl rings gave multiplets at τ 1.9–2.9. All integrations agreed with those expected from the structures. [b] Solvent = CCl₄. [c] Solvent = CDCl₃.

inum isopropoxide, and sodium methoxide from Matheson Coleman and Bell. Oxygen was passed through a tower of Drierite before use. Nitrogen was purified according to the method of Meites.[30]

The olefins, 2-methyl-2-butene and 2-methyl-1-butene, which were used as standards in gas–liquid chromatography, were obtained from Phillips Petroleum Company. The comparison samples of isobutene, *trans*-2-butene, and *cis*-2-butene were Matheson Coleman and Bell materials.

Equipment. A high-vacuum line was used for the trapping of olefinic products. Glc analyses of the olefinic mixtures were carried out on a Loenco Model 15B thermal conductivity instrument, and peaks integrated with a Disc integrator or planimeter. The following columns were employed for separation of olefins: column A, a 10-ft column packed with 20% dimethylsulfolane on 60–80 mesh Chromosorb P; column B, an 11-ft column packed with 20% triethylene glycol saturated with silver nitrate on 60–80 mesh Chromosorb P. The constant temperature bath was controlled to ±0.2°. Nmr spectra were at 60 MHz (Varian A-60) with $(CH_3)_4Si$ as internal standard.

Synthesis of Esters. The following two methods were used. Yields are in Table V.

Method A. A typical procedure is as follows. A mixture of isobutyl alcohol (0.046 mole) and pyridine (0.044 mole) was added dropwise to $(C_6H_5)_2P(O)Cl$ (0.042 mole). The resulting thick slurry was stirred for an additional 10 min, then washed into a separatory funnel with 75 ml of benzene and extracted with three 30-ml portions of H_2O, 30 ml of HCl, 30 ml of saturated $NaHCO_3$, and three 3-ml aliquots of H_2O. The benzene layer was dried over anhydrous K_2CO_3 and evaporated to white crystals, 80.5% yield, and recrystallized from acetone to give an analytical sample, mp 80–82°.

Method B. A typical procedure is as follows. $(C_6H_5)_2PCl$ (0.23 mole) in 250 ml of benzene was delivered into a dried flask. Dry O_2 was slowly introduced through a gas dispersion tube. Gentle refluxing of the solution was maintained by proper adjustment with nitrogen.[31] Sodium methoxide (9.77 g, 0.181 mmole)

Isolation of Products from Pyrolyses. Several procedures were used in order to obtain the data in Table I. The *tert*-butyl and isopropyl esters were heated in an electric furnace in a break-seal tube and the gaseous products were isolated on a vacuum line and analyzed by mass spectrometry. The solid product was shown to be diphenylphosphinic acid by melting point and mixture melting point. The isobutyl ester was pyrolyzed in a distilling flask connected to a trap at −80°. The olefins were carried into the trap by a stream of dry nitrogen, and the mixture was analyzed by glc using Matheson gases for comparison. The pinacolyl, neopentyl, and menthyl esters were pyrolyzed in an evacuated system. The ester was placed in a pyrolysis tube, and the entire apparatus was degassed and flushed with dry N_2. On pyrolysis, the olefins distilled into a trap which was kept at −195°. A subsequent transfer to a tared storage bulb enabled weighing and glc analysis of the products. Stability of the olefins under experimental conditions was demonstrated. The olefin mixture from the pinacolyl ester showed no isomerization over diphenylphosphinic acid under the experimental conditions for pyrolysis. The two olefins from pyrolysis of the neopentyl ester were heated individually in a closed system over diphenylphosphinic acid at 350° for 5 min and 3 min and each showed no isomerization. In the actual pyrolyses, the olefins are swept out of the melt in much shorter times.

Rate Studies. Samples of ester, hydroquinone, and diphenylphosphinic acid were weighed into a tared 18 × 150 mm tube. The sample was then immersed in the bath at the desired temperature. The tube was periodically removed from the bath, cooled, dried, and weighed. A theoretical weight of the tube at infinite time was calculated from the weight of the ester which was used. From the loss in weight of the sample tube, the percentage of unchanged ester and A/E could be calculated.

Partial Pyrolysis. Pinacolyl diphenylphosphinate (0.532 g, 1.76 mmoles) was pyrolyzed at 225.9° for 30 min (39% reaction).

(30) L. Meites and T. Meites, *Anal. Chem.*, **20**, 948 (1948).

(31) In one experiment in which the solution was not flushed with nitrogen, addition of a hot sodium isopropoxide solution resulted in an explosion. It is advisable to flush the flask with nitrogen after diphenylphosphinous chloride is oxidized with oxygen.

The pyrolysis tube was evacuated to remove olefinic products, the white, crystalline residue was triturated with deuteriochloroform, and the filtrate was examined by nmr. The only peaks present were those attributable to the pinacolyl ester. No peaks were observed which could be ascribed to the rearranged tertiary ester, 2,3-dimethyl-2-butyl diphenylphosphinate. Although this analysis is limited by the sensitivity of the method used, it appears to rule out any rearrangement of starting material as a source of rearranged olefin.

The Structure of the Product Obtained from an Unusual Phosphine Halogenation Reaction[1]
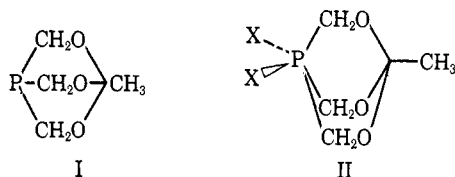
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Abstract: Single-crystal X-ray structural analysis of the bromination product of the bicyclic phosphine $P(CH_2O)_3$-CCH_3 shows that ring opening has occurred to form $(BrCH_2)_2P(O)CH_2OOCCH_3$. An unusual feature of the structure is that despite the bulkier substituents, the CPC bond angles range from 100 to 104° whereas those in $OP(CH_3)_3$ are 106°. This result is rationalized in terms of the isovalent hybridization hypothesis and the accommodation of the smaller CPC angles by an outward folding of the bromine and acetoxy groups with respect to the P=O axis. Also discussed are the ^1H, ^{31}P, and ^{13}C spectra and the signs and magnitudes of the $^{31}P-^{13}C$ and $^{31}P-^1H$ couplings determined from indor experiments. A plausible mechanism for the reaction is proposed.

Fluorination of trialkylphosphines yields pentacovalent phosphorus derivatives of the type X_2PR_3 in which the fluorines tend to occupy the axial positions of a trigonal bipyramid in the liquid or solution state.[3] Analogous products are probably also formed with chlorine and bromine as shown by their low conductivities in dilute acetonitrile,[4] the strong implication of their presence in the racemization of optically active trialkylphosphines,[5] and the zero dipole moments of X_2AsR_3 systems.[6] Dissociation into XPR_3^+ and X^- ions occurs when X is iodine and evidence has been presented for the presence of XPR_3^+ species in the solid state when X is Cl, Br, and I.[4]

Because the constraint in a bicyclic phosphine such as 1-phospha-4-methyl-3,5,8-trioxabicyclo[2.2.2]octane (I) could give rise to an unusual five-coordinate geome-

I   II

try for phosphorus as shown in II, we have undertaken the halogenation of I under a variety of conditions. We report here the reaction of I with bromine which yields $(BrCH_2)_2P(O)CH_2OOCMe$ (III) in high yield from room temperature to 0°. The formulation of this substance as shown is made definitive by the single-crystal X-ray diffraction study and supported by ^1H, ^{31}P, and ^{13}C nmr experiments.

Recently the reaction of chlorine with phosphetanes in dichloromethane was reported to give chlorophosphine derivatives,[7] an example being
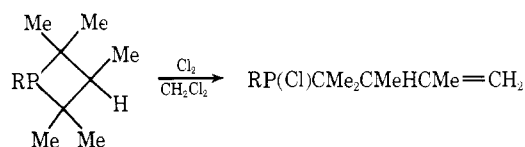
As in our reaction, ring opening is observed but in contrast, a phosphorus–carbon bond is broken, and only one halogen atom is incorporated into the product, while the other apparently removes a proton from a methyl group forming HCl.

Experimental Section

Bis(bromomethyl)acetoxyphosphine Oxide (III). To 10 ml of a 0.5 M benzene solution of I[8] kept under a flow of dry nitrogen was slowly added an equimolar amount of bromine dissolved in 20 ml of benzene. The addition was carried out at room temperature and, upon its completion, the clear solution was reduced to half its volume under vacuum. An equivalent volume of pentane was then added and the cloudy solution cooled to 0° for 1 hr. The white crystals collected by filtration were recrystallized from ether in 65% yield (mp 69°).

Anal. Calcd for $C_5H_9O_3Br_2P$: C, 19.49; H, 2.92; P, 10.07; Br, 51.92. Found: C, 19.71; H, 2.87; P, 9.14; Br, 49.76.

X-Ray Diffraction Study. Clear, colorless crystals of III were grown by slow evaporation of a methylene chloride–hexane solution. Microscopic examination revealed that the crystals were acicular with sharply defined faces. Crystals were selected and mounted on glass fibers. Preliminary Weissenberg photographs exhibited $2/m$ Laue symmetry indicating a monoclinic space group. The following systematic absences were observed: $h0l$ when $l = 2n + 1$, and $0k0$ when $k = 2n + 1$. These absences uniquely

(1) Contribution No. 3007. Work was performed in the Ames Laboratory of the Atomic Energy Commission and the Chemistry Department of Iowa State University.

(2) NSF Trainee.

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(4) K. Issleib and W. Seidel, *Z. Anorg. Allgem. Chem.,* **288**, 201 (1956).

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(6) K. A. Jensen, *Z. Anorg. Allgem. Chem.,* **250** 257 (1943).

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