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# The Mechanism of the Rearrangement of Bis(diphenylphosphinyl) Peroxide[1]

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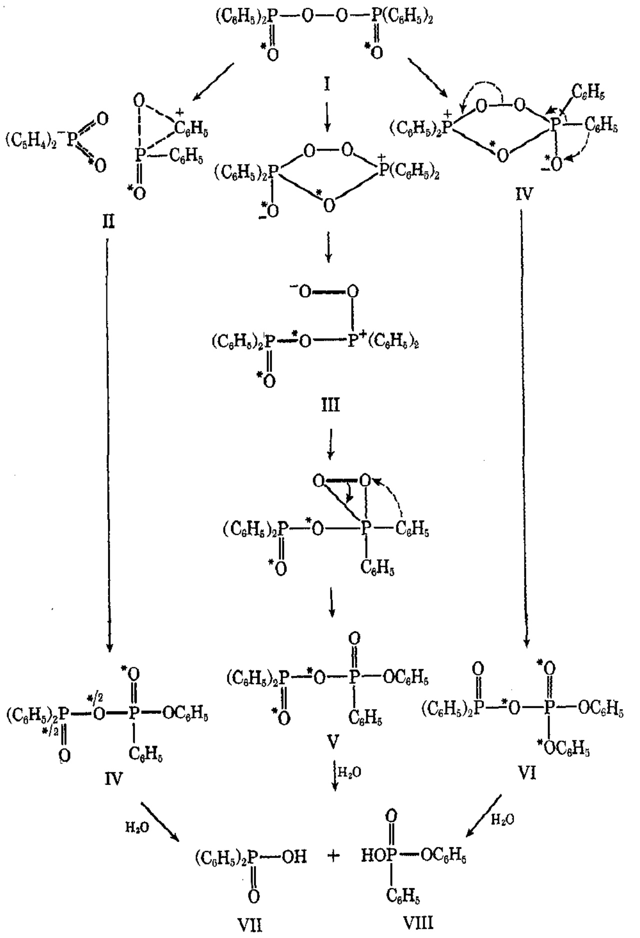
The thermal decomposition of bis(diphenylphosphinyl-$^{18}O$) peroxide in chloroform solution has been found to produce an unsymmetrical anhydride [$Ph_2P(=O)OP(=O)OPh_2$] in which all of the oxygen-18 label remains in the oxo oxygens. Only a concerted process or an ion pair so intimate as to prevent scrambling of the label is consistent with this labeling of the rearrangement product. In contrast, photolysis of the labeled peroxide in chloroform results in a much more rapid first-order decomposition which yields the same anhydride but with scrambling of the oxygen-18 label. This scrambling of the label corresponds to a free-radical intermediate for the photolytic process.

The thermal decomposition of bis(diphenylphosphinyl) peroxide (I) has been found[4] to yield, after hydrolysis of the reaction mixture, diphenylphosphinic acid (VII) and phenyl hydrogen phenylphosphonate (VIII). Evidence was presented that the reaction was ionic in nature and the following three alternative mechanisms (Chart I) were proposed. The present work was planned to establish whether one of these three mechanisms can be operative by labeling the oxo oxygens of the peroxide with oxygen-18 and determining the labeling in the product. The decomposition of the peroxide was also reported[4] to be accelerated by light and in the present work it was proposed, in addition, to elucidate this photolytic mechanism by oxygen-18 labeling experiments.

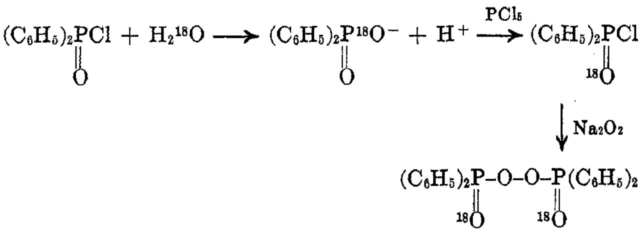
CHART I



appropriate labeling

## Results and Discussion

**Labeling of the Peroxide.**—Labeling of the peroxide was accomplished by the following sequence of reactions. Since the phosphinyl peroxide is thermally too unstable to pass through a mass spectrometer, the incorporation of oxygen-18 in the oxo oxygen of the peroxide was assumed to be identical with that in the precursor phosphinyl chloride.



$$(C_6H_5)_2\underset{\underset{O}{\|}}{P}Cl + H_2{}^{18}O \longrightarrow (C_6H_5)_2\underset{\underset{O}{\|}}{P}{}^{18}O^- + H^+ \xrightarrow{PCl_5} (C_6H_5)_2\underset{\underset{^{18}O}{\|}}{P}Cl \xrightarrow{Na_2O_2} (C_6H_5)_2\underset{\underset{^{18}O}{\|}}{P}\text{-}O\text{-}O\text{-}\underset{\underset{^{18}O}{\|}}{P}(C_6H_5)_2$$

Measurement of the oxygen-18 content of the diphenylphosphinyl chloride itself was found to be impractical, for the only peaks observed in the mass spectrometer corresponded to the chlorine cation (*m/e* 35, 37). However, treatment of the acid chloride with methanol gave the methyl ester which in the mass spectrometer produced a series of useful ions (Table I). The parent peaks (*m/e* 232, 234) were initially chosen for the analysis and, from the peak heights of multiple runs applying the statistical isotope occurrence formulas of Beynon,[5] the oxo oxygen enrichment with oxygen-18 above natural abundance was 5.3%. The base line at this portion of the spectrum was so poor and the correction for the m + 1 contribution of the 231 peak so large that the average

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[2] Taken in part from the thesis of R. L. Waller, submitted in May 1971, to the Graduate School, Case Western Reserve University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

[3] Preliminary work on this problem was performed at the American Cyanamid European Research Institute at Geneva, Switzerland.

[4] R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965).

[5] J. H. Beynon, "Mass Spectrometry and Its Applications to Organic Chemistry," Elsevier, Amsterdam, 1960, p 296.

TABLE I
IONS OBTAINED FROM UNLABELED METHYL DIPHENYLPHOSPHINATE IN THE MASS SPECTROMETER

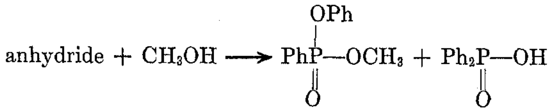
| Ion | $m/e$ | Relative peak heights |
|---|---|---|
| $(C_6H_5)_2POOCH_3^+$ | 232 | 54 |
| $(C_6H_5)_2POOCH_2^+$ | 231 | 100 |
| $(C_6H_5)_2PO^+$ | 201 | 22 |
| $C_6H_5POOCH_3^+$ | 155 | 29 |
| $C_6H_5^+$ | 77 | 52 |

deviation was at least 0.4%. Therefore the analysis was repeated using multiple runs of the peaks at $m/e$ 155, 157, where a satisfactory base line was obtained and there were no nearby peaks contributing. From the 155, 157 peaks, the enrichment of oxo oxygen with oxygen-18 was determined to be 4.6% with an average deviation of only 0.2%. The theoretical value from the enriched water (10.13% oxygen-18)[6] was 4.96%. The experimental value (4.6%) can be expected to be a little lower than the theoretical because of the inability to completely exclude atmospheric moisture during the synthesis. The labeled acid chloride was converted to the peroxide by the literature method.[4]

**Identification of the Anhydride Product.**—In the initial work with the phosphinyl peroxide,[4] it was concluded that the unsymmetrical anhydride (*e.g.*, V) was produced by thermal rearrangement of I because hydrolysis of the reaction mixture led to essentially quantitative yields of VII and VIII. All attempts in the initial and present work to isolate or synthesize an analytically pure sample of the anhydride have failed. The compound not only may be low melting but in addition probably has a tendency to partially disproportionate to symmetrical anhydrides.

However, in the present work, in the mass spectrum of the crude thermal rearrangement reaction mixture was found a principle peak ($m/e$ 434) which corresponds to the molecular weight of the unsymmetrical anhydride. There is no other compound logically expected to be present with this molecular weight.

Also, treatment of the crude reaction mixture with methanol gave IX. This ester (IX) is the expected principal product from methanolysis of the anhydride because solvolytic attack should predominate where there is reduced electron density on the phosphonic phosphorus as opposed to the phosphinic phosphorus. An anhydride structure must be present because the ester IX could not be obtained from the corresponding acid VIII under the experimental conditions.



$$\text{anhydride} + CH_3OH \longrightarrow Ph\overset{OPh}{\underset{O}{P}}{-}OCH_3 + Ph_2\underset{O}{P}{-}OH$$

IX VII

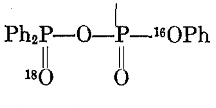
These two units of data therefore support the original conclusion that the unsymmetrical anhydride is the initial product of the rearrangement process.

**Determination of the Labeling in the Anhydride Produced by Thermal Rearrangement of the Peroxide.**—The labeled bis(diphenylphosphinyl) peroxide was thermally decomposed in chloroform solution and phenyl hydrogen phenylphosphonate (VIII) was isolated. This ester was cleaved with sodium naphthalene and the resultant phenol was transformed to the trimethylsilyl ether. Mass spectrometric analysis of this ether (Table II) disclosed that none of the oxygen-18 label was incorporated in the phenol oxygen.

Since the phenolic oxygen of VIII arises exclusively from the peroxidic oxygen of I, the rearrangement does not proceed through IV. Structures II and III are the only proposed intermediates consistent with these data.

In a preceding section of this paper an assumption was made that, in the conversion of the diphenylphosphinic chloride to the peroxide, there would be no scrambling of oxo and peroxidic oxygens. Such a scrambling to yield some oxygen-18 labeling of the peroxidic oxygens would necessarily produce some labeling of the phenolic oxygen of VIII. Therefore the absence of any oxygen-18 enrichment of the phenolic oxygen of VIII provides experimental proof that no scrambling of the label occurs during peroxide formation and this original assumption is experimentally confirmed.

To further elucidate the mechanism of the peroxide rearrangement, additional identification of the fate of the oxygen label was needed. The mass spectrum of a concentrated crude sample of the reaction products (Table III) provided two significant units of data. First, a principal peak ($m/e$ 434) was observed which corresponds to the molecular weight of the unsymmetrical anhydride. The importance of this peak in the proof of the anhydride structure has already been discussed. The second unit of data obtained from the mass spectrum of the reaction mixture was the measurement of a peak of $m/e$ 233 (Table II) corresponding to $PhOP({=}O)PhO^+$. The comparison of this peak to the 235 peak showed an oxygen-18 enrichment in this ion corresponding to the incorporation of only one oxygen-18 (4.5% enrichment of one oxygen found; 4.6% theoretical). The other oxygen-18 must necessarily be present in the anhydride as $Ph_2P{=}O$. Some confirmation of this conclusion was obtained by comparing the 201 peak to the 203 peak which showed the enrichment of oxygen-18 in this ion to be 4.9% above the natural abundance. This peak cannot correspond to the $PhOPPh^+$ ion because the phenolic oxygen has been proved not to be oxygen-18 enriched. In the $Ph_2PO^+$ ion, the oxygen logically arises from the $P{=}O$ linkage although the P—OP linkage as a source of this oxygen is not excluded. Therefore the labeling in both ions is in agreement with the following anhydride labeling.



$$Ph_2\underset{^{18}O}{P}{-}O{-}\overset{Ph}{\underset{O}{P}}{-}{}^{16}OPh$$

To establish the labeling of the last two undesignated oxygens, it was necessary to subject the crude rearrangement product to methanolysis to give methyl phenyl phenylphosphonate (IX). The importance of this solvolysis in proof of the anhydride structure has been discussed already. Mass spectral analysis of the $m/e$ 248 to the 250 peak of IX showed the presence of one labeled oxygen (3.8 ± 0.4% oxygen-18 enrichment found for one oxygen *vs.* 4.6% theoretical). The peak required for analysis was not a major peak (Table IV) and this accounts for the somewhat limited

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(6) Analysis provided by the $H_2{}^{18}O$ source, Miles Laboratories.

TABLE II

ISOTOPE RATIOS FOR REAGENTS AND PRODUCTS FROM THERMAL AND PHOTOLYTIC REARRANGEMENTS OF I

| Compd | Ion | Run | No. of scans | (M + 2)/M | Total $^{18}O$, % | $^{18}O$ enrichment, % |
|---|---|---|---|---|---|---|
| Methyl diphenylphosphinate[a] | $(C_6H_5)_2POOCH_3^+$ | 1 | 12 | 0.067 ± 0.0027 | 5.5[b] | 5.3[b] |
| Methyl diphenylphosphinate[a] | $C_6H_5P(O)OCH_3^+$ | 1 | 10 | 0.0531 ± 0.0011 | 4.8[b] | 4.6[b] |
| Phenyl trimethylsilyl ether[a] | $C_6H_5OSi(CH_3)_2^+$ | 1 | 10 | 0.0438 ± 0.0009 | 0.20 | 0 |
| Phenyl trimethylsilyl ether[a] | $C_6H_5OSi(CH_3)_2^+$ | 2 | 10 | 0.0437 ± 0.0009 | 0.18 | 0 |
| Unsymmetrical anhydride[a] | $C_6H_5OP(C_6H_5)OO^+$ | 1 | 6 | 0.0620 ± 0.0025 | 5.1[b] | 4.5[b] |
| Unsymmetrical anhydride[a] | $(C_6H_5)_2PO^+$ | 1 | 1 | 0.060 | 5.1 | 4.9 |
| Methyl phenyl phenylphosphonate[a] | $(C_6H_5)P(OC_6H_5)(O)(OCH_3)^+$ | 1 | 10 | 0.0542 ± 0.0043 | 4.4[b] | 3.8[b] |
| Phenyl trimethylsilyl ether[c] | $C_6H_5OSi(CH_3)_2^+$ | 1 | 10 | 0.0628 ± 0.0025 | 2.1 | 1.9 |

[a] Thermal rearrangement product. [b] $^{18}O$ enrichment only in one oxygen. [c] Photolytic rearrangement product.

TABLE III

MASS SPECTRAL ANALYSIS OF DIPHENYLPHOSPHINIC PHENYLPHOSPHINIC ANHYDRIDE PHENYL ESTER

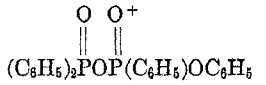
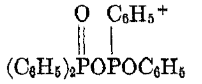
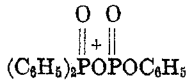
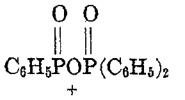
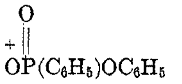
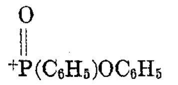
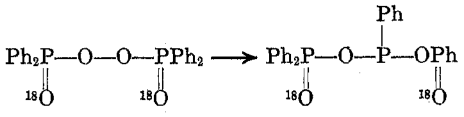
| Ion | *m/e* | Relative peak heights (parent *m/e* as 100) |
|---|---|---|
|  $(C_6H_5)_2\overset{\overset{O}{\parallel}}{P}O\overset{\overset{O^+}{\parallel}}{P}(C_6H_5)OC_6H_5$ | 434 | 100 |
|  $(C_6H_5)_2\overset{\overset{O}{\parallel}}{P}O\overset{\overset{C_6H_5^+}{\mid}}{P}OC_6H_5$ | 418 | 320 |
|  $(C_6H_5)_2\overset{\overset{O}{\parallel}}{P}\overset{+}{O}\overset{\overset{O}{\parallel}}{P}OC_6H_5$ | 357 | 610 |
|  $C_6H_5\overset{\overset{O}{\parallel}}{P}\underset{+}{O}\overset{\overset{O}{\parallel}}{P}(C_6H_5)_2$ | 341 | 1300 |
|  $\overset{+}{O}\overset{\overset{O}{\parallel}}{P}(C_6H_5)OC_6H_5$ | 233 | 14 |
|  $^+\overset{\overset{O}{\parallel}}{P}(C_6H_5)OC_6H_5$ | 217 | 210 |
| $(C_6H_5)_2PO^+$ | 201 | 300 |

TABLE IV

MASS SPECTRAL ANALYSIS OF METHYL PHENYL PHENYLPHOSPHONATE

| Ion | *m/e* | Relative peak heights (parent *m/e* as 100) |
|---|---|---|
| $(C_6H_5)(C_6H_5O)P(O)(OCH_3)^+$ | 248 | 100 |
| $(C_6H_5)(C_6H_5O)P(O)(OCH_2)^+$ | 247 | 126 |
| $(C_6H_5)(C_6H_5O)P(O)_2^+$ | 233 | 250 |
| $(C_6H_5)(C_6H_5O)P^+$ | 201 | 194 |
| $(C_6H_5O)P(O)(OCH_3)^+$ | 171 | 74 |
| $(C_6H_5)P(O)(OCH_3)^+$ | 155 | 525 |
| $(C_6H_5)P(OCH_3)^+$ | 139 | 115 |
| $C_6H_5O^+$ | 93 | 7550 |
| $C_6H_5^+$ | 77 | 7550 |

accuracy of this determination. The oxo oxygen must contribute this label, for the methoxy oxygen comes from the methanol and the phenoxy oxygen has been proved not to be labeled. The labeling pattern of the anhydride is now completely established. All three

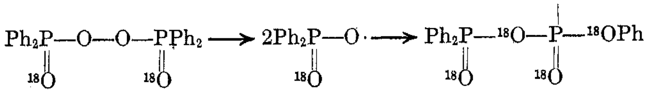


of the previously proposed[4] mechanisms are therefore incorrect. Instead there must be a concerted rearrangement or an ion pair similar to II so intimate that scrambling of the oxygen in the negative ion does not occur. A concerted rearrangement involves orbital symmetry restrictions which are difficult to evaluate because of the unsaturated groups adjacent to the reaction site.

**Photolytic Rearrangement of I.**—It has also been reported[4] that the rearrangement of I can be catalyzed by ultraviolet light. A free-radical mechanism was proposed for this rearrangement.

In the present work it was confirmed that the decomposition of I can be catalyzed by light because at 18° the half-life was only 7 min with the Hanovia lamp used, while without irradiation the half-life at this temperature was almost 10 hr. Obviously the photolytic mechanism differs from the thermal process. Previously[4] the photolytic process (with poor temperature control) was reported to be second order with respect to peroxide, but in the present work (with fairly good temperature control, 17 ± 1°) a good first-order plot was obtained.

Photolytic decomposition of I labeled with oxygen-18 as previously described has now been found to produce phenyl hydrogen phenylphosphinate in which the phenoxy group contains essentially one-half the enrichment (1.9 ± 0.4% above natural abundance) of oxygen-18 compared to the original oxo oxygen enrichment (4.6%). The 1.9 ± 0.4% compares favorably with the 2.3% predicted theoretically by complete oxygen scrambling in a free-radical intermediate.



The yields of rearrangement products were lower in the photolytic process than in the thermal reaction. Such low yields are often characteristic of free-radical intermediates.

## Experimental Section

**Diphenylphosphinic-$^{18}O$ Chloride.**—Diphenylphosphinic chloride (35.4 g, 0.15 mol) in benzene (100 ml) was refluxed for 1 hr with $H_2{}^{18}O$ (3 g, 0.16 mol). Diphenylphosphinic acid (35 g, 100% yield) was collected by filtration and dried to yield the pure acid, mp 188–190° (lit.[7] mp 190–191°). To the acid (17.6 g, 0.08 mol) mixed with phosphorus pentachloride (16.8 g, 0.08 mol) was added 1 ml of benzene and a vigorous reaction occurred. Vacuum distillation produced diphenylphosphinic-$^{18}O$ chloride (15.7 g, 88%), bp 165° (0.17 mm) [lit.[8] bp 158–160° (0.1 mm)].

The mass spectrum[9] of this compound had peaks only at $m/e$ 35 and 37.

**Methyl Diphenylphosphinate-*oxo*-$^{18}O$.**—A dry methanol (15 ml) solution of diphenylphosphinic-$^{18}O$ chloride (0.2 g) was refluxed overnight. The excess methanol was removed using a rotary evaporator and the residue was distilled to yield a viscous liquid, bp 141–143° (0.34 mm) [lit.[10] bp 139–140° (0.34 mm)]. After several hours the liquid gave crystals, mp 59–62°, which gave ir and nmr spectra identical with those previously reported[10,11] for the ester.

**Bis(diphenylphosphinyl-$^{18}O$) Peroxide.**—Diphenylphosphinic-$^{18}O$ chloride (15.5 g, 0.06 mol) in toluene (25 ml) was added slowly (45 min) at 0° to sodium peroxide (6.0 g, 0.077 mol) in water (100 ml). The mixture was stirred for 15 min after the addition was complete and the phosphinyl peroxide was then collected by filtration and washed first with cold (0°) water and then with small (2–5 ml) quantities of cold (0°) acetone. The crude peroxide was then dissolved in cold chloroform, heptane was added, and the mixture was cooled to give bis(diphenylphosphinyl-$^{18}O$) peroxide (6.1 g, 42%) which melted at 80° (lit.[4] mp 88°).

**Decomposition of the Labeled Peroxide amd Analysis of the Product.**—A solution of bis(diphenylphosphinyl-$^{18}O$) peroxide (6.1 g, 0.025 mol) in chloroform (75 ml) was stirred at room temperature overnight. The chloroform was evaporated *in vacuo* and the viscous residue was refluxed for 1 hr with a mixture of benzene (30 ml) and water (10 ml). The hot benzene layer was separated and evaporated. The crystalline residue was extracted with three 40-ml portions of boiling heptane. Cooling the combined heptane extracts precipitated phenyl hydrogen phenylphosphonate (2 g) which was collected by filtration and dissolved in tetrahyhrofuran (20 ml). Addition of sodium–naphthalene (0.03 mol) in tetrahydrofuran (20 ml) produced a vigorous reaction. When the reacton had subsided, the tetrahydrofuran was evaporated, the residue was dissolved in 0.1 *M* aqueous potassium hydroxide (20 ml), and the alkaline solution washed with three 30-ml portions of ether. The raffinate was acidified to pH 6 and extracted with three 40-ml portions of ether. The combined ether extracts were dried with magnesium sulfate and evaporated. The residue was refluxed for 1 hr with hexamethyldilazane (3 ml) and a trace of sand. Distillation yielded a liquid (1 ml) whose infrared spectrum was identical with that of authentic trimethylsilylphenyl ether. Mass spectral analysis of the ethers from two separate runs (Table II) using multiple scans of the $m/e$ peaks 151 and 153, gave an oxygen-18 to oxygen-16 ratio for the phenolic oxygen of 0.0020 and 0.0018 (average 0.0019). Since the natural abundance is 0.0020, there was no oxygen-18 enrichment of the phenolic oxygen.

**Methanolysis of Diphenylphosphinic Phenylphosphonic Anhydride Phenyl Ester Produced from the Thermal Decomposition of I in Chloroform.**—A solution of I (2 g) in chloroform (100 ml) was stirred overnight at room temperature. An aliquot (10 ml) was added to anhydrous methanol (5 ml) and the resulting solution was refluxed overnight. Evaporation of this solution produced a viscous oil which was dissolved in ether (20 ml) and the ether solution was washed once with 5% aqueous sodium bicarbonate. Acidification of the basic extract produced diphenylphosphinic acid (0.85 g, mp 190°) which from the infrared spectrum appeared to contain small quantities of phenyl hydrogen phenylphosphonate. The ether raffinate was dried (Drierite) and evaporated to yield a viscous oil which gave infrared and nmr spectra identical with an authentic sample of methyl phenyl phenylphosphonate. In a control experiment, replacement of the aliquot with VIII gave no IX.

A second aliquot (10 ml) of the decomposition mixture was refluxed with methanol (5 ml) overnight, the mixture was concentrated by evaporating solvent, and the residue was subjected directly to mass spectral analysis.

A third aliquot of the reaction mixture was subjected directly to mass spectral analysis to observe the principal peak for the anhydride and the peaks corresponding to the ions produced by its fragmentation.

**Kinetic Measurement of the Photolytic Decomposition of I.**—The peroxide absorbs radiation at 275 mμ (ε 6300), 267 (7480), and 242 (15,900). A solution of bis(diphenylphosphinyl-$^{18}O$) peroxide (0.02 mol) in chloroform (1000 ml) was placed in a liquid-cooled immersion uv reactor. The system was irradiated with a mercury vapor lamp employing a Corex filter which prevented light below 260 ml from entering the reaction mixture. The temperature was maintained at 17 ± 1°. Aliquots were withdrawn at regular intervals and added to sodium iodide in 1:4 acetic acid–isopropyl alcohol, the resultant mixture was refluxed for 2 min, and the liberated iodine was titrated with standard sodium thiosulfate solution. With this photolytic apparatus, duplicate runs gave good first-order plots corresponding to a rate constant of $1.55 \pm 0.02 \times 10^{-2}\ \mathrm{sec}^{-1}$. The kinetic figures in minutes and ln $a/(a - x)$ are, respectively, 3, 0.000; 5, 0.1750; 7, 0.3750; 9, 05871; 13, 1.000; 18, 1.3748; 22, 1.7437.

**Photolytic Decomposition of Labeled I.**—The above apparatus was utilized with I (6 g) in chloroform (1000 ml). The system was purged with nitrogen and then irradiated for 1 hr at 17°. The chloroform was distilled and the residue was refluxed for 4 hr with benzene (40 ml) and water (10 ml). The benzene layer was separated and evaporated. The residue was extracted with three 40-ml portions of boiling heptane. Cooling the combined heptane extracts gave VIII (0.6 g) which was cleaved with sodium naphthalene and converted to phenyl trimethylsilyl ether by the method already described. The ether was then subjected to mass spectral analysis.

**Registry No.**—Bis(diphenylphosphinyl) peroxide, 4250-08-2.

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[7] A Michaelis and F. Wegner, *Ber.*, **48**, 316 (1915).

[8] N. T. Kurnath, Ph.D. Thesis, Case Western Reserve University, 1970.

[9] All the mass spectra were determined on a Varian M-66 mass spectrometer and are accurate to about ±5% for a major peak, but with ±10% for a minor peak or a poor base line.

[10] K. D. Berlin, T. H. Austin, and K. L. Stone, *J. Amer. Chem. Soc.*, **86**, 1787 (1964).

[11] K. D. Berlin, T. H. Austin, and M. Nagabhushanam, *J. Org. Chem.*, **30**, 1267 (1965).