one concerted step to form IV and CH_3OH. A linear dependence on methoxide ion concentration would be expected, except as it might be modified by salt effects. We cannot exclude this possibility on the basis of our present results, but we consider it unlikely because no strong catalysis of this type has been encountered in other aromatic nucleophilic substitutions involving amine reagents.

Bunnett and Bernasconi[4] found reaction 1 in 10% dioxane–90% water to exhibit curvilinear dependence of k_A on hydroxide ion concentration. Their study was conducted at constant ionic strength, and the curvature could not be attributed to a salt effect. Comparison of the two studies shows that the relative rates of reversion of intermediate III to reactants and progression to products are altered by change of solvent and base.

By the principle of microscopic reversibility, the reverse of reaction 1 must occur by the same mechanism, in the other direction. The reverse mechanism in Chart I is a reasonable one.

Registry No.—I, 119-27-7; II, 839-93-0; methanol, 67-56-1; piperidine, 110-89-4; sodium methoxide, 124-41-4.

The Reaction of Diphenylphosphinous Chloride with Benzoyl Peroxide[1]

GEORGE SOSNOVSKY AND DAVID J. RAWLINSON

University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

Received December 19, 1967

The reaction of equimolar quantities of diphenylphosphinous chloride, Ph_2PCl (1), and benzoyl peroxide in refluxing benzene produces a mixture of benzoyl chloride, benzoic anhydride, and diphenylphosphinic anhydride, $Ph_2P(O)OP(O)Ph_2$ (**2**). In addition, a mixed anhydride, $PhC(O)OP(O)Ph_2$ (**3**), is detected. The first step of the reaction is an oxygen transfer from peroxide to **1** to form benzoic anhydride and diphenylphosphinyl chloride (4) In a secondary reaction **4** interacts with benzoic anhydride to give a mixture of benzoyl chloride, **3**, and benzoic anhydride. Mixed anhydride is thus not a primary product but is formed by a metathesis between benzoic anhydride and **4** or/and by an equilibration of benzoic anhydride with **2**.

The reaction between peroxides and trivalent phosphorus compounds may proceed by either a homolytic or a heterolytic route, or by a combination of the two, the products giving some indication of the favored route.[2-4] Thus, the reaction of benzoyl peroxide with triphenyl or tri-*n*-butyl phosphine (eq 1, R = Ph, *n*-Bu)

$$PhC(O)OO(O)CPh + R_3P \longrightarrow PhC(O)O(O)CPh + R_3P \rightarrow O \quad (1)$$

yields the corresponding phosphine oxide and benzoic anhydride,[5,6] the net effect being the transfer of an oxygen atom to phosphorus. In this case the involvement of ionic intermediates is established.[7,8] However, a radical mechanism is thought to operate in the reaction of phosphorus trichloride with benzoyl peroxide to yield carbon dioxide, benzoyl chloride, and benzene phosphonyl dichloride[9] (eq 2). Benzoyl peroxide and

$$PhC(O)OO(O)CPh + PCl_3 \longrightarrow PhC(O)Cl + PhP(O)Cl_2 + CO_2 \quad (2)$$

triethyl phosphite react in solution by the ionic route to yield benzoic anhydride and triethyl phosphate (eq 1, R = OEt), but the uncontrolled reaction in the absence of a solvent yields in addition to these products diethyl-phenyl phosphonate, $PhP(O)(OEt)_2$, indicating, at least in part, a homolytic route.[10]

Recently, we reported[1b] that the reaction of benzoyl peroxide with diphenylphosphinous chloride (1), although not homolytic, is apparently different from the general ionic type expressed by eq 1. There were isolated benzoyl chloride, and two symmetrical anhydrides, benzoic anhydride and diphenylphosphinic anhydride (2) (eq 3). In addition, a mixed benzoic

$$\underset{\mathbf{1}}{Ph_2PCl} + PhC(O)OO(O)CPh \longrightarrow PhC(O)Cl + {}^1/_2PhC(O)O(O)CPh + {}^1/_2\underset{\mathbf{2}}{Ph_2P(O)O(O)PPh_2} \quad (3)$$

diphenylphosphinic anhydride (3) was detected but was not isolated in pure form. This paper outlines in

$Ph_2P(O)O(O)CPh$
3

greater detail the results of the preliminary communication, and provides further information about the reaction path and the role of **3** in the reaction.

Results

In initial preparative-scale experiments, the reaction between **1** and benzoyl peroxide was carried out in refluxing benzene at molar concentration. Under these conditions and after an isolation procedure involving distillation and recrystallization, the final products were identified as benzoyl chloride, benzoic anhydride, and **2**. The stoichiometry corresponds roughly to eq 3. In addition, another material with a characteristic ir absorption band in the carbonyl region at 1740 cm^{-1} (which is not displayed by the other carbonyl-containing materials in the system) was detected in the

---

[1] (a) This investigation was supported by a grant from the Public Health Service, U. S. Department of Health, Education, and Welfare (GM 14932-01). The preliminary results (b) were published in *Chem. Ind.* (London), 120 (1967) and (c) were presented in part in a talk at the International Symposium on the Chemistry of Organic Peroxides in Berlin, DDR, Sept 1967.

[2] J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).

[3] R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press Inc., New York, N. Y., 1965, Chapters 6 and 9.

[4] C. Walling and M. S. Pearson in "Topics in Phosphorus Chemistry," Vol. III, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, Inc., New York, N. Y., 1966, p 18.

[5] F. Challenger and V. K. Wilson, *J. Chem. Soc.*, 213 (1927).

[6] L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

[7] M. A. Greenbaum, D. B. Denney, and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **78**, 2563 (1956).

[8] D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

[9] M. Karelsky and K. H. Pausacker, *Aust. J. Chem.*, **11**, 336 (1958).

[10] A. J. Burn, J. I. G. Cadogan, and P. J. Bunyan, *J. Chem. Soc.*, 1527 (1963).

reaction mixture during work-up and as a contaminant of crops of low-melting **2** obtained from the mother liquor. Several attempts, using varying work-up procedures, to isolate a pure sample of this material from the peroxide reaction were unsuccessful.

The hitherto unknown anhydride **3** was prepared by the reaction of diphenylphosphinic acid and benzoyl chloride in the presence of 2,6-lutidine (lu), and its physical properties and chemical behavior under the conditions of the peroxide reaction were established. Comparison of ir spectra of pure **3** with those of samples of **2** from the peroxide reaction containing material with a band at 1740 cm^{-1} established that the latter material was **3**.

$$Ph_2P(O)OH + PhC(O)Cl + lu \longrightarrow \underset{\mathbf{3}}{Ph_2P(O)O(O)CPh} + lu \cdot HCl$$

In addition to identification of products, the following observations were made. No gas (CO_2, HCl) was evolved, and neither chlorobenzene nor biphenyl was detected. The product composition was identical both in the presence and absence of catalytic amounts of cupric bromide.

Ir spectra indicated that under the chosen conditions the reaction of benzoyl peroxide with **1** proceeded rapidly. No rate measurements were therefore made under these conditions. Immediately after the addition of benzoyl peroxide, benzoic anhydride and only minor quantities of benzoyl chloride and **2** were present. As refluxing continued, the amounts of benzoyl chloride and **2** increased at the expense of the benzoic anhydride. Compound **3** could not be positively identified until the removal of benzoyl chloride by distillation.

Thus, there were clear indications that, after an initial rapid reaction, secondary interactions of the products in the reaction mixture, and possibly also during the isolation procedure, had occurred.

In order to clarify the reaction path, the reaction conditions were changed. At room temperature and in more dilute solution, the initial interaction of benzoyl peroxide and **1** was slowed down to a rate which allowed the study of the disappearance of the reactants, and the appearance of the primary products. No attempt was made to isolate the products, because it was by now known that further interaction occurs during distillation and recrystallization procedures. Instead, extensive use was made of ir spectra in following the changes and identification of products.

Under these conditions the primary products are diphenylphosphinyl chloride (**4**) and benzoic anhydride, which do not rapidly react further. However, on refluxing they were converted into the final product mixture consisting of benzoyl chloride, benzoic anhydride, and **2**. Thus, a clean separation was achieved between the initial interaction of benzoyl peroxide with **1** (eq 4), and the further interactions of the primary products, benzoic anhydride and **4** (eq 5). Additional evidence was obtained from the reaction of **4** with benzoic anhydride. The reaction of a synthetic mixture of these reactants proceeded only slowly at room temperature, and gave products identical with those obtained from benzoyl peroxide at reflux.

$$\underset{\mathbf{1}}{Ph_2PCl} + PhC(O)OO(O)CPh \longrightarrow \underset{\mathbf{4}}{Ph_2P(O)Cl} + PhC(O)O(O)CPh \quad (4)$$

$$\underset{\mathbf{4}}{Ph_2P(O)Cl} + PhC(O)O(O)CPh \longrightarrow PhC(O)Cl + \underset{\mathbf{2}}{{}^1/_2Ph_2P(O)O(O)PPh_2} + {}^1/_2PhC(O)O(O)CPh \quad (5)$$

Further work at room temperature and high dilution showed that inhibitors, such as galvinoxyl and diphenylpicrylhydrazyl (DPPH), and also catalytic amounts of cupric bromide, have no effect on the rate or products of the reaction between benzoyl peroxide and **1**. Each of the "stable" free radicals interacted with **1**, as evidenced by a change in color and the simultaneous disappearance of the esr signal of the radical. However, the reaction mixtures still markedly inhibited the otherwise rapid autoxidation of **1**.

Each reaction system, with and without inhibitors or cupric bromide, behaved identically when the initially formed products at room temperature were refluxed. Benzoyl chloride, benzoic anhydride, and **2** were the products in each case. A synthetic mixture of **4** and benzoic anhydride at the same concentration also yielded the same mixture of products.

Further evidence was sought bearing on the role of **3** in the reaction. Careful examination of the ir spectra of samples from the reaction of benzoyl peroxide with **1** and those of synthetic mixtures of **4** and benzoic anhydride after refluxing in benzene was not conclusive because of the close proximity of the carbonyl absorptions of benzoyl chloride and **3**. It could only be concluded that **3** might be present in minor quantities. After removal of solvent and benzoyl chloride by distillation, the carbonyl peak (1740 cm^{-1}) of **3** was now clearly distinguishable. If benzoic anhydride was now removed by distillation, **3** remained as the only carbonyl-containing material in the residue, but again only in minor quantities.

A solution of **3** in refluxing benzene rapidly transformed to an equilibrium mixture containing the two symmetrical anhydrides and an appreciable proportion of **3**. The same equilibrium mixture was reached more slowly when equimolar amounts of benzoic anhydride and **2** were refluxed in benzene. The behavior at room temperature was similar, and the transformation of **3** yielded an equilibrium mixture containing a rather larger proportion of **3**.

In refluxing benzene, the two systems, **4**–benzoic anhydride and **3**–benzoyl chloride, are transformed to the same equilibrium mixture, identical with that obtained from the reaction of benzoyl peroxide with **1** (eq 3).

Each system after equilibration gave an identical mixture of products, namely benzoyl chloride, benzoic anhydride, **2**, and traces of **3** during the isolation procedure. The equilibrium does not lie completely to the right as shown by eq 3, since small changes occur when a mixture of the composition shown is refluxed in benzene.

Equilibrium in refluxing benzene was reached within 4 hr, except for the reaction of **3** with benzoyl chloride. In this case the decomposition of **3** was slower than the decomposition of **3** alone under the same conditions.

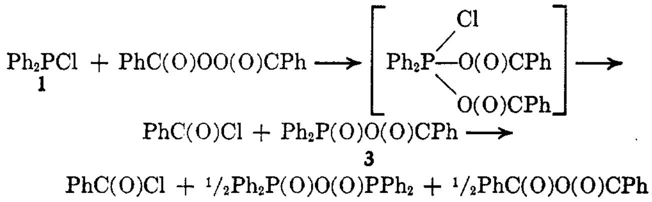
Discussion

The pathway and mechanism of the reaction of benzoyl peroxide with **1** are of interest because of the apparently different behavior from the reactions of triphenylphosphine and phosphorus trichloride.

The detection of **3**, unstable with respect to the corresponding symmetrical anhydrides, led us initially to

$$\mathrm{Ph_2P(O)O(O)CPh} \rightleftarrows \tfrac{1}{2}\mathrm{Ph_2P(O)O(O)PPh_2} + \tfrac{1}{2}\mathrm{PhC(O)O(O)CPh}$$

the conclusion that **3** might be an important intermediate in the reaction. The formation of **3** could be rationalized through participation of a pentacovalent phosphorus addition compound, as has been discussed in other cases.[3]



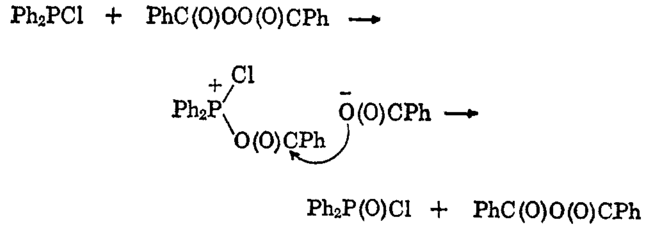
This assumption was disproved by experiments at room temperature, which showed that successive steps are involved, described by eq 4 and 5.

Compound **3** is clearly not an intermediate in the initial interaction of **1** and benzoyl peroxide, but is formed at some later stage.

The first step (eq 4) is formally identical with the reaction path observed in the case of the reaction of triphenylphosphine with benzoyl peroxide, *i.e.*, an oxygen transfer. The inhibition data obtained at room temperature seem to exclude a radical mechanism. This conclusion is supported also by the absence of an effect of copper salts, and the autoxidative data. It has been shown[11,12] that traces of copper salts can drastically change the rates and products of radical reactions of peroxy compounds. The absence of such an effect in the reaction of benzoyl peroxide with **1** indicates that a radical path may not be operative.

Inhibition of autoxidation of **1** by galvinoxyl and DPPH clearly demonstrates that this autoxidation is a radical process. The observation that **1** is rapidly autoxidized independent of the presence of benzoyl peroxide indicates that the radical species involved in the autoxidation play no part in the peroxide reaction.

It is probable then that the first step (eq 4) proceeds through an ionic mechanism such as that established for the reaction of triphenylphosphine.



The data obtained at low temperatures do not necessarily apply rigorously to the high temperature conditions, where a radical process could be partially operative. In this case, the absence of carbon dioxide in the products, inertness of the solvent, and the lack of effect of copper salts on product composition, seem also to exclude a radical mechanism.

The second step (eq 5) consists of the metathesis between **4** and benzoic anhydride. Compound **3** was not conclusively identified in this process, and if present would only be in small concentration. Separate experiments with **3** show that it decomposes to an equilibrium mixture with the two symmetrical anhydrides. It is proposed that **3** is an unstable intermediate in the second step, for which the following reaction path

$$\underset{\mathbf{4}}{\mathrm{Ph_2P(O)Cl}} + \mathrm{PhC(O)O(O)CPh} \longrightarrow \mathrm{PhC(O)Cl} + \underset{\mathbf{3}}{[\mathrm{PhC(O)O(O)PPh_2}]}$$

$$\underset{\mathbf{3}}{[\mathrm{Ph_2P(O)O(O)CPh}]} \rightleftarrows \underset{\mathbf{2}}{\tfrac{1}{2}\mathrm{Ph_2P(O)O(O)PPh_2}} + \tfrac{1}{2}\mathrm{PhC(O)O(O)CPh}$$

might be applicable, since it is difficult otherwise to visualize a simple one-step process which satisfies the overall stoichiometry of eq 5.

$$\mathrm{Ph_2P(O)Cl} + \tfrac{1}{2}\mathrm{PhC(O)O(O)CPh} \longrightarrow \tfrac{1}{2}\,\mathrm{Ph_2P(O)O(O)PPh_2} + \mathrm{PhC(O)Cl}$$

Abundant references can be found in the literature supporting the generality of this type of interaction of acid halides with anhydrides. Thus acetic anhydride reacts with carboxylic acid chlorides[13,14] to yield the corresponding carboxylic anhydride and acetyl chloride. For example, the reaction of acetic anhydride with benzoyl chloride[13] produces an almost quantitative yield of benzoic anhydride; the presumed intermediate, acetic benzoic anhydride, which is thermally unstable,[15] is not isolated. However, the reaction of acetic anhydride with chlorides of nonmetal or metalloid chlorides may proceed only as far as a mixed anhydride which is thermally stable and can be isolated. For example, acetates result from the reaction of acetic anhydride with phosphoryl chloride,[16] silicon tetrachloride,[17] aluminum chloride,[18] and chlorodiphenylboron.[19]

$$\mathrm{MeC(O)O(O)CMe} + \mathrm{PhC(O)Cl} \rightleftarrows \mathrm{MeC(O)Cl} + [\mathrm{MeC(O)O(O)CPh}]$$

$$[\mathrm{MeC(O)O(O)CPh}] \rightleftarrows \tfrac{1}{2}\mathrm{MeC(O)O(O)CMe} + \tfrac{1}{2}\mathrm{PhC(O)O(O)CPh}$$

$$\mathrm{P(O)Cl_3} + 3\mathrm{MeC(O)O(O)CMe} \longrightarrow \mathrm{P(O)[O(O)CMe]_3} + 3\mathrm{MeC(O)Cl}$$

$$\mathrm{SiCl_4} + 4\mathrm{MeC(O)O(O)CMe} \longrightarrow \mathrm{Si[O(O)CMe]_4} + 4\mathrm{MeC(O)Cl}$$

$$\mathrm{AlCl_3} + \mathrm{MeC(O)O(O)CMe} \longrightarrow \mathrm{AlCl_2[O(O)CMe]} + \mathrm{MeC(O)Cl}$$

$$\mathrm{Ph_2BCl} + \mathrm{MeC(O)O(O)CMe} \longrightarrow \mathrm{Ph_2BO(O)CMe} + \mathrm{MeC(O)Cl}$$

---

(11) G. Sosnovsky and S. O. Lawesson, *Angew. Chem. Intern. Ed. Engl.*, **3**, 269 (1964).

(12) S. O. Lawesson and G. Sosnovsky, *Svensk Kem. Tidskr.*, **75**, 343 (1963).

(13) F. Zetsche, *et al.*, *Helv. Chim. Acta*, **9**, 177 (1926).

(14) N. O. V. Sonntag, J. R. Trowbridge, and I. J. Krens, *J. Amer. Oil Chem. Soc.*, **31**, 151 (1954).

(15) W. Autenrieth and G. Thomae, *Chem. Ber.*, **57**, 423 (1924).

(16) C. L. Wale, *Chem. Ind.* (London), 2003 (1963).

(17) V. V. Udovenko and Yu. Ya. Fialkov, *Zh. Obshch. Khim.*, **27**, 905 (1957); *Chem. Abstr.*, **52**, 3712*d* (1958).

(18) J. Boeseken and F. Meijer Cluwen, *Rec. Trav. Chim. Pays-Bas*, **31**, 367 (1912).

(19) B. M. Mikhailov and N. S. Fedorov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 857 (1958); *Chem. Abstr.*, **53**, 1203*f* (1959).

The comparative ease of detection of **3** from the peroxide reaction during work-up after removal of solvent may be due to a more favorable equilibrium in the absence of solvent. A similar situation has been recorded recently[20] involving the interaction of acetic anhydride with **2**.

Experimental Section

Melting and boiling points are uncorrected. The molecular weight determination was carried out by Rast's method. Elemental microanalyses were performed by MicroTech Laboratories, Skokie, Ill.

Diphenylphosphinous chloride, benzoyl peroxide, benzoyl chloride, benzoic anhydride, 2,6-lutidine, cupric bromide, galvinoxyl, and diphenylpicrylhydrazyl (DPPH) were commercial products. Diphenylphosphinyl chloride was prepared by air oxidation of neat diphenylphosphinous chloride[21] at 130° in 36 hr, followed by distillation at reduced pressure. Diphenylphosphinic acid was prepared by the reaction of diphenylphosphinous chloride with aqueous alkaline hydrogen peroxide.[22] Diphenylphosphinic anhydride was made by the reaction of diphenylphosphinic acid with diphenylphosphinyl chloride[23] in the presence of base, *e.g.*, 2,6-lutidine.

All experiments were carried out under nitrogen where appropriate, with exclusion of atmospheric moisture. No gas evolution was observed in the peroxide reactions.

Peroxide in the reaction mixtures could not be estimated by direct iodometric titration after addition of sodium iodide and a catalyst. Instead, ir spectra were used to follow the progress of the reactions and to confirm the characterization of isolated materials. Standard spectra were prepared for comparison purposes. The main absorption bands for each material are listed in Table I, with an indication (*) (low intensity bands have been omitted) of those bands which were most useful for characterization. Identification of mixtures was confirmed where possible by comparing spectra with those of synthetic mixtures.

Table I

Compounds	Ir absorptions, cm^{-1}
Ph_2PCl	1430, 1090*, 740*
$Ph_2P(O)Cl$	1435, 1250, 1235, 1120, 750, 725
$PhC(O)OO(O)CPh$	1785*, 1765*, 1595, 1450, 1220, 1175, 995
$PhC(O)O(O)CPh$	1785, 1725, 1600, 1450, 1210, 1170, 1010*, 995*, 775
$PhC(O)O(O)PPh_2$	1740*, 1450, 1435, 1260–1240 (sh), 1235, 1205, 1165, 1125, 1070, 1020–1040, 1015, 835*, 770, 745, 720
$PPh_2(O)O(O)PPh_2$	1440, 1245, 1130, 1110, 1000, 945*, 745, 725
$PhC(O)Cl$	1770, 1730, 1590, 1580, 1450, 1200, 1170, 870*, 775
$PhC(O)OH$	2500–3200*, 1690*, 1450, 1415, 1320, 1290

Reaction of Benzoyl Peroxide with Diphenylphosphinous Chloride (1) A. In Refluxing Benzene. a. In the Presence of Cupric Bromide.—Benzoyl peroxide (24.2 g, 0.1 mol) suspended in benzene (50 ml) was added dropwise during 1 hr to a refluxing solution of **1** (18 ml, 0.1 mol) and cupric bromide (0.2 g, 0.9 mmol) in benzene (50 ml). After an exothermic reaction, the mixture was refluxed for a further 3 hr. The solvent was then removed at 14 mm, and the residual oil was distilled and yielded benzoyl chloride (7.6 g, 0.0543 mol), bp 100–110° (50 mm); benzoic anhydride (10.0 g, 0.0442 mol), bp 100–138° (0.05 mm), mp 43–44.5° (ether–petroleum ether, 20–40°); and a residue. Successive crops of **2** were obtained by recrystallization of the residue from benzene and repeated addition of ether to the evaporated mother liquor to precipitate further solid material. Obtained were crop 1 (3.2 g), mp 145–148°, crop 2 (9.0 g), mp 138–143°, and crop 3 (5.0 g), mp 137–140°, to total 17.2 g (0.041 mol).

b.—Experiment a was repeated with more detailed ir monitoring of the reaction and a slight variation in work-up procedure. After the addition period (1 hr) the characteristic peaks of benzoyl peroxide (1765, 1220, and 1175 cm^{-1}) and that of **1** (1090 cm^{-1}) were not observed. Instead, benzoic anhydride (two peaks of almost equal intensity at 1010 and 995 and carbonyl absorption at 1785 cm^{-1}) and smaller proportions of benzoyl chloride (870 cm^{-1}) and **2** (945 cm^{-1}) could be detected. After refluxing for 3 hr more, the ir spectrum indicated the formation of more **2** and benzoyl chloride at the expense of benzoic anhydride, which was, however, still present. Alkaline hydrolysis of an aliquot followed by acidification and removal of insoluble diphenylphosphinic acid by filtration produced an aqueous solution which was then titrated against silver nitrate. The titration indicated that all chlorine could be converted by hydrolysis into chloride ion. After removal of benzoyl chloride (7.8 g, 0.0553 mol), bp 75° (13 mm), the ir spectrum of the residual oil showed carbonyl absorptions of similar intensity at 1780, 1740, and 1725 cm^{-1}. Crystallization of the residual oil from benzene yielded **2** (8.0 g, 0.0191 mol), mp 146–146.5°. Ether treatment of the evaporated mother liquor yielded a brownish solid (5.5 g), mp 125.5–148°; the ir spectrum of this material showed that it was **2** contaminated with anhydride **3** (only one absorption band in the carbonyl region at 1740 cm^{-1}). Evaporation of the mother liquor gave a dark residual oil (15.3 g). The ir spectrum of this oil indicated that it consisted of a mixture of benzoic anhydride with a small proportion of **2**, benzoyl chloride, and benzoic acid.

c. In the Absence of Cupric Bromide.—Experiment a, repeated with the omission of cupric bromide, gave essentially identical results. There were isolated benzoyl chloride (8.4 g, 0.060 mol), bp 105–115° (35 mm); benzoic anhydride (9.9 g, 0.0438 mol), bp 140° (0.2 mm), mp 44–44.5° (ether–petroleum ether); **2** (successive crops totaling 19.0 g, 0.045 mol); and a residue.

B. The Primary Process. Formation of Diphenylphosphinyl Chloride (4) and Benzoic Anhydride in Benzene at Room Temperature. a. In the Absence of Cupric Bromide.—A solution of benzoyl peroxide (2.42 g, 0.01 mol) in benzene (25 ml) was added to a stirred solution of **1** (2.0 ml, 2.44 g, 0.011 mol) in benzene (25 ml) at room temperature, and samples of the reaction mixture were removed periodically for ir analysis. The reaction was conducted in an atmosphere of nitrogen, and the benzene used was previously purged with nitrogen. The temperature of the reaction mixture rose from 29 to 36.5° during about 30 min; thereafter, the reaction mixture slowly cooled down to room temperature. During the first hour the slow disappearance of peroxide was followed through the decreasing intensity of the carbonyl peak at 1765 cm^{-1}. After 5 hr peroxide was not detectable, and the spectrum was completely superimposable on that of an equimolar mixture of **4** and benzoic anhydride in benzene at the same dilution.

b. In the Presence of Cupric Bromide.—The preceding experiment a, repeated in the presence of catalytic amounts of cupric bromide (0.90 mmol), produced no change in either rate or composition of products.

c. In the Presence of DPPH and Galvinoxyl.—Stock solutions of DPPH (10^{-2} *M*) and galvinoxyl (5×10^{-3} *M*) were made up in benzene which had been purged with nitrogen, and used within 12 hr. The color of DPPH stock solution (purple) was unchanged over several days, but that of galvinoxyl (brown) faded appreciably over 24 hr. When **1** (2.0 ml, 0.011 mol) was added to the stirred benzene stock solution (25 ml) of radical, a rapid (about 1 min) color change occurred, from purple to brown for DPPH, and from brown to yellow for galvinoxyl. After the color change had occurred, no esr signal was detectable in either reaction mixture.

The preceding experiment a was now repeated. The benzene solution of benzoyl peroxide was added to the resulting reaction mixture (from addition of **1** to the benzene solution of radical), in which the color change was complete and no esr signal was detectable. The ir spectra throughout the reaction, in the case of each radical, were identical with those in the absence of these additives. Thus, within the limits of the experimental method, there was no inhibition of rate or changes of products.

Inhibition of Autoxidation of Ph_2PCl (1) to $Ph_2P(O)Cl$ (4).—A solution of **1** (0.01 mol) in benzene (50 ml), which was purged with nitrogen, was stirred under a nitrogen atmosphere, and

---

(20) D. L. Venezky and C. F. Poranski, Jr., *J. Org. Chem.*, **32**, 838 (1967).

(21) P. Hauke and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966).

(22) L. R. Ocone, *et al.*, *U. S. Dept. Comm. Office Tech. Serv.*, *AS 262*, 806 (1961); *Chem. Abstr.*, **59**, 2853*h* (1963).

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

oxygen was introduced at a rate of about two bubbles per second. An exothermic reaction occurred, and the conversion of **1** into **4** was completed within 20 min (by ir).

When the experiment was repeated with the addition of benzoyl peroxide (0.01 mol) just before the introduction of oxygen, the autoxidation was completed within 15 min, while benzoyl peroxide remained unaffected.

The autoxidation was now attempted with the reaction mixture resulting from addition of **1** (0.01 mol) to the benzene solution (25 ml) of DPPH, in which the color change was complete, and no esr signal was detectable. No autoxidation occurred. In the case of galvinoxyl (1×10^{-3} *M*), a strong retardation was observed.

C. The Secondary Process. Reaction of Benzoic Anhydride with Diphenylphosphinyl Chloride (4) in Benzene at Reflux.—The ir spectra of the mixtures of products obtained in experiments B (a–c) remained unchanged over a period of a few hours at room temperature. On heating at reflux for 24 hr all mixtures produced the following result. The ir spectra indicated that **2** (945 cm^{-1}) and benzoyl chloride (870 cm^{-1}) were formed at the expense of benzoic anhydride (1010 and 995 cm^{-1}), which, however, was still detectable. The spectra were identical with those of an equimolar mixture of **4** and benzoic anhydride at the same concentration which had been refluxed for 24 hr and were also identical with those of a mixture of a composition of benzoyl chloride (1.0 mol), **2** (0.5 mol), and benzoic anhydride (0.5 mol) at the same concentration which had been refluxed for 4 hr.

Preparation of Mixed Anhydride, PhC(O)O(O)PPh$_2$ (3).—Benzoyl chloride (42 g, 0.3 mol) was added over 10 min to a stirred solution of diphenylphosphinic acid (65 g, 0.3 mol) and 2,6-lutidine (32 g, 0.3 mol) in dry benzene (500 ml) below 25°. The apparatus was protected from atmospheric moisture. After 3 hr at 25°, the reaction mixture was filtered. The ir spectrum of the filtrate showed only one absorption peak (1740 cm^{-1}) in the carbonyl region. On evaporation of benzene under reduced pressure, there were obtained crop 1 (29.5 g), mp 113.5–115.5°; crop 2 (23 g), mp 119–120°; crop 3 (12.8 g) mp 121–140°; and an oily residue (24.2 g). Four recrystallizations of crop 1 from benzene at 10° yielded pure **3**, mp 123.5–124°. Material obtained by recrystallization from benzene tenaciously retained solvent, and melted rather low (110–120°). On pumping at 0.1 mm pressure for 12 hr the melting point rose to 123–124°.

Anal. Calcd for $C_{19}H_{15}O_3P$: C, 70.79; H, 4.69; mol wt, 322. Found: C, 70.63; H, 4.80; Mol wt, 320.

The ir spectrum showed only one peak in the carbonyl region (1740 cm^{-1}). Other strong absorption bands are at 1450, 1435, 1260–1240 (sh), 1235, 1205, 1165, 1125, 1070, 1020–1040, 1015, 835, 770, 745, and 720 cm^{-1}. Low intensity absorptions are at 1518 and 1105 cm^{-1}.

When this reaction was repeated at higher temperatures a mixture of the three anhydrides was produced from which pure **3** could not be readily separated.

Decomposition of 3 in Refluxing Benzene.—Compound **3** was generated in solution by the previously described reaction between **4** (23.6 g, 0.1 mol), benzoic acid (12.2 g, 0.1 mol), and 2,6-lutidine (10.7 g) in benzene (200 ml). The white suspension was refluxed for 4 hr, and 2,6-lutidine hydrochloride (13.3 g, 0.093 mol) was removed by filtration. Solvent was then removed at reduced pressure, and the residual oil was distilled to yield benzoic anhydride (6.8 g, 0.0301 mol): bp 125–143° (0.02 mm); mp 42–43.5° (ether–petroleum ether). Recrystallization of the pot residue from benzene and precipitation with ether yielded **2**: crop 1 (13.2 g, 0.0316 mol), mp 145–146.5°; crop 2 (4.4 g), mp 131–139.5°; crop 3 (1.2 g), mp 125–137°; and a residue (3.7 g). Ir spectra of crops 2 and 3 indicated that they contained traces of **3**.

The preceding experiment was repeated in order to follow the progress of the reaction by ir spectroscopy. A solution of **3** (3.2 g, 0.01 mol), mp 123–124°, in benzene (15 ml) was refluxed. After 15 hr the ir spectrum indicated the formation of a mixture of benzoic, diphenylphosphinic, and mixed anhydrides at equilibrium; *i.e.*, the ir spectrum was not significantly altered on refluxing for a further 24 hr. The equilibrium mixture is composed of approximately equal molar amounts of the three anhydrides.

Decomposition of 3 in Benzene at Room Temperature.—A solution of **3** (3.2 g, 0.01 mol), mp 123–124°, in benzene (15 ml) was left at room temperature protected from atmospheric moisture, and the progress of the decomposition followed by taking ir spectra. The rate of decomposition was slower than that in refluxing benzene. After 24 hr, slightly more **3** remained than was present in the equilibrium mixture at reflux. After 48 hr, a little more decomposition had occurred, but the amount of **3** was still slightly greater than that at reflux in benzene.

Reaction of Benzoic Anhydride and Diphenylphosphinic Anhydride (2) in Refluxing Benzene.—A solution of benzoic anhydride (2.26 g, 0.01 mol), mp 44–44.5°, and **2** (4.20 g, 0.01 mol) in benzene (30 ml) was refluxed, and the progress of the reaction was followed by ir spectroscopy. After 3 hr at reflux the ir spectrum indicated that about 65% of the benzoic anhydride remained and a corresponding amount of **3** (about 0.006 mol) had appeared. The spectrum was not altered by further reflux and corresponded to the same equilibrium mixture which was formed from **3** dissolved in benzene at reflux.

The final spectra from each experiment were completely superimposable.

Reaction of 3 with Benzoyl Chloride in Refluxing Benzene.—Compound **3** was generated in solution by the previously described reaction between diphenylphosphinic acid (2.18 g, 0.1 mol), benzoyl chloride (28.2 g, 0.2 mol), and 2,6-lutidine (10.7 g, 0.1 mol) in benzene (125 ml). The white suspension was refluxed for 4 hr, and lutidine hydrochloride (13.1 g, 0.092 mol) was removed by filtration. Solvent was then removed at reduced pressure, and the residual oil was distilled to yield benzoyl chloride (8.0 g, 0.0567 mol), bp 73° (11 mm), and benzoic anhydride (5.2 g, 0.023 mol), bp 125–140° (0.03 mm), mp 46° (ether–petroleum ether). Recrystallization from benzene and precipitation with ether yielded **2**: crop 1 (9.7 g, 0.0232 mol), mp 144.5–145.5°; crop 2 (1.4 g), mp 144–146°; crop 3 (3.4 g), mp 127–147°; and a residue (5.7 g). Ir spectra of crops 2 and 3 indicated that they consisted of **2** contaminated with **3**. The residue consisted of benzoic anhydride with a considerable proportion of **3**.

The reaction of benzoyl chloride with **3** was repeated on a smaller scale in order to follow the reaction by ir spectroscopy. A solution of benzoyl chloride (2.81 g, 0.02 mol) and **3** (6.44 g, 0.02 mol) in benzene (40 ml) was refluxed. After 4 hr, the benzoyl chloride (870 cm^{-1}) concentration remained unchanged, but **3** had decomposed to benzoic anhydride and **2**. Within the wide limits of the experimental method, not more than 50% of **3** had decomposed. The reaction had not come to equilibrium, however, since after 15 hr further decomposition of **3** had occurred, although a considerable proportion still remained.

Reaction between Diphenylphosphinyl Chloride (4) and Benzoic Anhydride.—A solution of benzoic anhydride (11.3 g, 0.05 mol) and **4** (11.8 g, 0.05 mol) in benzene (50 ml) was refluxed for 4 hr. The ir spectrum indicated the appearance of benzoyl chloride and some **2** at the expense of the benzoic anhydride. No clear conclusion could be drawn at this stage concerning the presence of **3**. After removal of the solvent, benzoyl chloride (4.4 g, 0.0312 mol), bp 70–73° (12 mm), was distilled. The ir spectrum of the residue indicated a mixture of the three anhydrides. Benzoic anhydride (5.4 g, 0.0239 mol), bp 134–136° (0.12 mm), mp 42–45°, was then removed by distillation. Recrystallization of the residue yielded **2**: crop 1 (5.1 g, 0.0122 mol), mp 147.5–148°; crop 2 (2.8 g, 0.0067 mol), mp 134–141°; and a residue (2.3 g). The ir spectrum indicated that crop 1 consisted of pure **2**, crop 2 was the same material contaminated with **3** (1740-cm^{-1} absorption), and the residue was a mixture of **2**, **3**, and benzoic anhydride.

Reaction between Benzoyl Chloride, Benzoic Anhydride, and Diphenylphosphinic Anhydride (2).—A mixture of benzoyl chloride (2.81 g, 0.02 mol), benzoic anhydride (2.26 g, 0.01 mol), and **2** (4.20 g, 0.01 mol) dissolved in benzene (40 ml) was refluxed. The progress of the reaction was followed by ir spectroscopy. Only minor changes occurred during a 4-hr period; a very small decrease in concentration of each reactant occurred, together with appearance of small shoulders at about 1740 and 835 cm^{-1}. It could only be concluded that **3** could not be present in more than very small proportions if present at all.

Registry No.—**1**, 1079-66-9; **2**, 5849-36-5; **3**, 4693-63-4; **4**, 1499-21-4; benzoyl peroxide, 94-36-0.

Acknowledgments.—The authors wish to thank The Stauffer Chemical Co. and Lucidol Division, Wallace and Tiernan, Inc., for samples of diphenylphosphinous chloride and benzoyl peroxide.