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288. *The Reactivity of Organophosphorus Compounds. Part XV.*[1] *Reactions of Diaroyl Peroxides with Triethyl Phosphite.*

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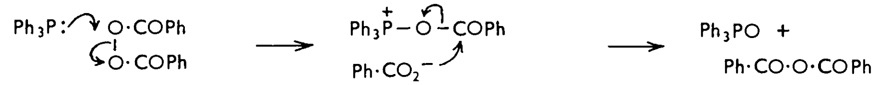
Contrary to earlier reports, dibenzoyl peroxide does not initiate a reaction between triethyl phosphite and chloroform or carbon tetrachloride. Triethyl phosphite and dibenzoyl peroxide react vigorously in chloroform, carbon tetrachloride, or ether to give good yields of benzoic anhydride and triethyl phosphate, probably by heterolysis. The uncontrolled reaction, in the absence of solvent, gives diethyl phenylphosphonate in addition to the above products, thus suggesting homolysis in this case. Prolonged reaction of the phosphite and the peroxide in chloroform gives hexaethyl benzylidynetriphosphonate, $[(EtO)_2P(O)]_3CPh$, formed by way of benzoic anhydride.

Reduction of peroxides by organic tervalent phosphorus compounds occurs by either a heterolytic or a homolytic route according to the nature of the peroxides involved.[2] For instance, reaction of dibenzoyl peroxide with triphenylphosphine, shown by Challenger and Wilson [3] to give benzoic anhydride and triphenylphosphine oxide, proceeds by way



of ion pairs in ether.[4] Reduction of dialkyl peroxides by triethyl phosphite or triphenylphosphine, on the other hand, involves homolysis of the peroxidic bond; the alkoxy-radicals formed are rapidly deoxygenated by way of an intermediate radical, in which the phosphorus shell has expanded to nine electrons, as follows: [5-7]

$$\begin{aligned} &RO{\cdot}OR \longrightarrow 2RO{\cdot} \\ &RO{\cdot} + (EtO)_3P \longrightarrow (EtO)_3\dot{P}{\cdot}OR \longrightarrow (EtO)_3PO + R{\cdot} \\ &R{\cdot} \longrightarrow \text{products} \end{aligned}$$

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[1] Part XIV, Bunyan and Cadogan, *J.*, 1963, 42.

[2] Cadogan, *Quart. Rev.*, 1962, XVI, 208.

[3] Challenger and Wilson, *J.*, 1927, 209.

[4] Denney and Greenbaum, *J. Amer. Chem. Soc.*, 1957, **79**, 979; Denney, Greenbaum, and Hoffmann, *ibid.*, 1956, **78**, 2563.

[5] Horner and Jurgeleit, *Annalen*, 1955, **591**, 138.

[6] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

[7] Walling, Basedow, and Savas, *J. Amer. Chem. Soc.*, 1960, **82**, 2181.

Similar phosphoranyl radicals have been postulated as intermediates in radical-induced reactions of polyhalogenomethanes and alkanethiols with triethyl phosphite,[6,8,9] *e.g.*:

$$\cdot CCl_3 + (EtO)_3P \longrightarrow (EtO)_3\dot{P}\cdot CCl_3 \xrightarrow{BrCCl_3} [(EtO)_3P\cdot CCl_3]^+Br^- + \cdot CCl_3$$

$$[(EtO)_3P\cdot CCl_3]^+Br^- \longrightarrow \underset{(I)}{(EtO)_2P(O)\cdot CCl_3} + EtBr$$

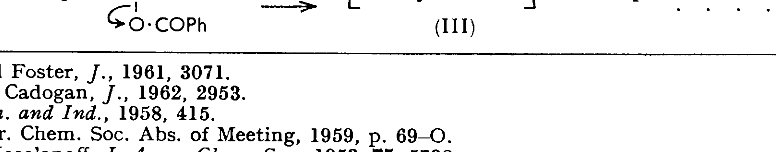
Diethyl trichloromethylphosphonate (I) can similarly be formed from triethyl phosphite and carbon tetrachloride; Griffin [10] has stated that dibenzoyl peroxide can be used to initiate this reaction, and assumed, on the basis of an acceleration in the reaction in the presence of the peroxide, that homolysis of the peroxide occurred. Cadogan and Foster,[8] while agreeing that reaction could proceed under certain conditions by a homolytic route, noted however that the acceleration in the presence of dibenzoyl peroxide was only two-fold, and that the possibility could not be ignored of heterolytic reaction between the phosphite and peroxide in a manner analogous to the corresponding reaction between triphenylphosphine and dibenzoyl peroxide. The suspicion that dibenzoyl peroxide is an ineffective initiator for homolytic reactions in triethyl phosphite was further noted by Bunyan and Cadogan.[2,9] Recently, however, this possibility appeared to be discounted when Griffin [11] reported (without experimental detail) that dibenzoyl peroxide effectively initiated a radical reaction between chloroform and triethyl phosphite, which do not react in the absence of additives.[12] Further, it was claimed that reaction between the initial product, diethyl dichloromethylphosphonate (II), and benzoyloxy-radicals also occurred to give a product formulated as $(EtO)_2P(O)\cdot CCl_2\cdot O_2CPh$.

$$(EtO)_3P + CHCl_3 \longrightarrow (EtO)_2P(O)\cdot CHCl_2\ (II) + EtCl$$

The investigation described in this paper was accordingly undertaken in an attempt to resolve these anomalies by the determination of the course and mechanism of the reaction of dibenzoyl peroxide with triethyl phosphite both in the absence and in the presence of added solvents such as chloroform.

When dibenzoyl peroxide was added to three equivalents of triethyl phosphite under nitrogen, a violent reaction occurred after an induction period. The products after 15 minutes included benzoic anhydride, triethyl phosphate, ethyl benzoate, and a small amount of diethyl phenylphosphonate (identified by gas–liquid chromatography). The reaction was less complex when carried out under rigorous conditions of cooling and gave high yields of triethyl phosphate and benzoic anhydride. Diethyl phenylphosphonate was not formed in this instance and the reaction was not vigorous. Smooth reaction to give benzoic anhydride (81%) and triethyl phosphate (97%) also occurred when equimolar amounts of the reactants were boiled under reflux in ether for 90 minutes; diethyl phenylphosphonate was not formed during this reaction. High conversions into the corresponding anhydrides and triethyl phosphate were similarly effected from di-*p*-chlorobenzoyl and di-*p*-bromobenzoyl peroxide. Benzoyl *p*-nitrobenzoyl peroxide under these conditions gave benzoyl *p*-nitrobenzoyl anhydride (85%), the symmetrical anhydrides not being formed.

In theory, benzoic anhydride can be formed from dibenzoyl peroxide by both homolytic and heterolytic routes, in the latter case by way of nucleophilic attack on a peroxidic oxygen atom to give an intermediate ion pair (III), thus:



$$(EtO)_3P:\ \begin{matrix} O\cdot COPh \\ | \\ O\cdot COPh \end{matrix} \longrightarrow \underset{(III)}{\left[(EtO)_3P\cdot O\cdot COPh\right]^+}\ PhCO_2^- \quad . \quad . \quad . \quad . \quad (i)$$

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[8] Cadogan and Foster, *J.*, 1961, 3071.

[9] Bunyan and Cadogan, *J.*, 1962, 2953.

[10] Griffin, *Chem. and Ind.*, 1958, 415.

[11] Griffin, Amer. Chem. Soc. Abs. of Meeting, 1959, p. 69–O.

[12] Crofts and Kosolapoff, *J. Amer. Chem. Soc.*, 1953, **75**, 5738.

Subsequent debenzoylation of the cation then gives benzoic anhydride and triethyl phosphate [reaction (ii)]. Alternatively, de-ethylation of the cation (III) to give ethyl benzoate and benzoyl diethyl phosphate (IV) is also possible [reaction (iii)]:

$$\mathrm{(EtO)_3\overset{+}{P}\cdot O\cdot COPh\ Ph\cdot CO_2^-} \longrightarrow \begin{cases} \mathrm{(EtO)_3PO + Ph\cdot CO\cdot O\cdot COPh} & \ldots\ldots \text{(ii)} \\ \mathrm{(EtO)_2P(O)\cdot O\cdot COPh\ (IV) + Ph\cdot CO_2Et} & \ldots \text{(iii)} \end{cases}$$

The ethyl benzoate isolated from these reactions is believed, however, to result from reaction of benzoic anhydride with triethyl phosphite as discussed below, since the amount of ester increases on prolonged heating of the reaction mixture after the initial reaction between peroxide and phosphite is complete. Moreover, the other possible product of reaction (iii), benzoyl diethyl phosphate (IV) and its possible transformation product, tetraethyl pyrophosphate, are not formed.

Homolytic reaction of triethyl phosphite with dibenzoyl peroxide would be expected to proceed by way of an intermediate benzoyloxyphosphoranyl radical (V), formed either by reaction of benzoyloxy-radicals with triethyl phosphite or by a displacement of a benzoyloxy-radical by reaction of the phosphite at the peroxidic bond. In view of the well-known tendency for dibenzoyl peroxide to undergo induced decompositions of this type, the latter is more likely at low temperatures.

Thus, both mechanisms will account for the formation of benzoic anhydride, triethyl phosphate, and ethyl benzoate, but the formation of diethyl phenylphosphonate can be accommodated only by a homolytic mechanism. On the other hand, the formation of only the unsymmetrical anhydride in the reaction of triethyl phosphite and benzoyl *p*-nitrobenzoyl peroxide in ether is considered to be compatible only with a heterolytic route:

$$\begin{aligned}
\mathrm{(EtO)_3P + Ph\cdot CO\cdot O\cdot O\cdot COPh} &\longrightarrow \mathrm{(EtO)_3\dot{P}\cdot O\cdot COPh + Ph\cdot CO_2\cdot} \\
\mathrm{(EtO)_3P + Ph\cdot CO_2\cdot} &\longrightarrow \mathrm{(EtO)_3\dot{P}\cdot O\cdot COPh\ (V)} \\
\mathrm{(EtO)_3\dot{P}\cdot O\cdot COPh + Ph\cdot CO\cdot O\cdot O\cdot COPh} &\longrightarrow \mathrm{[(EtO)_3P\cdot O\cdot COPh]^+Ph\cdot CO_2^-\ (III) + Ph\cdot CO_2\cdot} \\
\mathrm{[(EtO)_3P\cdot O\cdot COPh]^+Ph\cdot CO_2^-} &\longrightarrow \mathrm{(EtO)_3PO + Ph\cdot CO\cdot O\cdot COPh} \\
\mathrm{(EtO)_3\dot{P}\cdot O\cdot COPh} &\longrightarrow \mathrm{(EtO)_3PO + Ph\cdot CO\cdot} \\
\mathrm{Ph\cdot CO\cdot + Ph\cdot CO\cdot O\cdot O\cdot COPh} &\longrightarrow \mathrm{PhCO\cdot O\cdot COPh + Ph\cdot CO_2\cdot} \\
\mathrm{(EtO)_3P + Ph\cdot CO\cdot} &\longrightarrow \mathrm{(EtO)_3\dot{P}\cdot COPh} \longrightarrow \mathrm{(EtO)_2P(O)\cdot COPh + Et\cdot} \\
\mathrm{Et\cdot + Ph\cdot CO\cdot O\cdot O\cdot COPh} &\longrightarrow \mathrm{Ph\cdot CO_2Et + Ph\cdot CO_2\cdot} \\
\mathrm{Ph\cdot CO_2\cdot} &\longrightarrow \mathrm{Ph\cdot + CO_2} \\
\mathrm{Ph\cdot + (EtO)_3P} &\longrightarrow \mathrm{(EtO)_3\dot{P}\cdot Ph} \longrightarrow \begin{cases} \mathrm{(EtO)_2P(O)Ph + Et\cdot} \\ \mathrm{[EtO)_3PPh]^+Ph\cdot CO_2^- + Ph\cdot CO_2\cdot} \end{cases} \\
\mathrm{[(EtO)_3PPh]^+Ph\cdot CO_2^-} &\longrightarrow \mathrm{(EtO)_2P(O)Ph + Ph\cdot CO_2Et}
\end{aligned}$$

Homolysis, being less selective, would lead to all three anhydrides:

$$\mathrm{2Ar\cdot CO\cdot O\cdot O\cdot COPh + 2(EtO)_3P} \longrightarrow \mathrm{[(EtO)_3P\cdot O\cdot COAr]^+Ph\cdot CO_2^- + Ar\cdot CO_2\cdot}$$
$$\mathrm{+\ [(EtO)_3P\cdot O\cdot COPh]^+Ar\cdot CO_2^- + Ph\cdot CO_2\cdot,\ etc.}$$

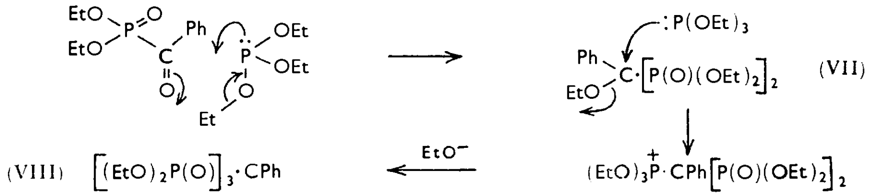
The experimental observations therefore suggest that reactions in ether between diaroyl peroxides and triethyl phosphite proceed by heterolysis, whereas the uncontrolled high-temperature reaction in the absence of solvent indicates homolysis, at least in part.

This explanation rests, therefore, on a change in mechanism according to reaction conditions. On this basis it would be expected that benzoyl *p*-nitrobenzoyl peroxide, which gives only the unsymmetrical anhydride by the heterolytic route in ether, should give all three possible anhydrides in the uncontrolled reaction. This was observed, but the result is of doubtful significance since under the conditions of this reaction the unsymmetrical anhydride equilibrates to give a mixture of all three possible anhydrides.

Reactions carried out in carbon tetrachloride or chloroform parallel those carried out in ether. Thus an equimolar mixture of triethyl phosphite and dibenzoyl peroxide in an excess of carbon tetrachloride gave, after 10 minutes, benzoic anhydride (99%) and triethyl phosphate (97%). Diethyl trichloromethylphosphonate was not formed during this time but was formed slowly *after* the peroxide had been consumed. It is clear, therefore, that, whatever the mechanism of its reaction with triethyl phosphite, dibenzoyl peroxide does not initiate the reaction between triethyl phosphite and carbon tetrachloride.

In view of Griffin's claim that diethyl dichloromethylphosphonate is formed on reaction of dibenzoyl peroxide and triethyl phosphite in chloroform, this reaction has now been extensively investigated. It has been shown that chloroform and triethyl phosphite alone do not react in 18 hours at the b. p. Moreover, diethyl dichloromethylphosphonate was not formed in reactions involving a two- or four-fold excess of chloroform over phosphite in the presence of small initiator-amounts of dibenzoyl peroxide (0·01—0·05 mole/mole of phosphite). Gas–liquid chromatography, which would have detected very small quantities (~0·1%) of diethyl dichloromethylphosphonate, of the products of these reactions indicated small quantities of triethyl phosphate equivalent to the amount of peroxide used, together with small quantities of ethyl benzoate. It is therefore probable that such reaction as occurred involved only the phosphite and peroxide to give triethyl phosphate and benzoic anhydride [reaction (ii)], *chloroform merely acting as a solvent.* In order to confirm the presence of benzoic anhydride and to establish the mode of formation of ethyl benzoate, experiments (42 hr. reflux) were carried out with larger proportions of peroxide: diethyl dichloromethylphosphonate or chlorine-containing products were not formed, thus confirming the non-participation of chloroform in the reaction. In addition, benzoic anhydride, triethyl phosphate, and ethyl benzoate were isolated together with a high-boiling compound, formulated as hexaethyl benzylidynetriphosphonate (VIII). It follows, therefore, that, under the above conditions of reaction, triethyl phosphite reacts with dibenzoyl peroxide to give triethyl phosphate and benzoic anhydride as discussed above; the latter is then assumed to undergo nucleophilic attack by triethyl phosphite to give ethyl benzoate and diethyl benzoylphosphonate (VI). This in turn undergoes reaction with more phosphite at the carbonyl carbon atom to give the intermediate αα-bisdiethoxyphosphorylbenzyl ethyl ether (VII), which reacts further with triethyl phosphite to give the observed ester (VIII).

$$(EtO)_3P + Ph{\cdot}CO{\cdot}O{\cdot}COPh \longrightarrow (EtO)_3\overset{+}{P}{\cdot}COPh\ Ph{\cdot}CO_2^- \longrightarrow \underset{(VI)}{(EtO)_2P(O){\cdot}COPh} + Ph{\cdot}CO_2Et$$



This rationalisation is supported by the following observations: (*a*) Triethyl phosphite and benzoic anhydride are known[13] to give diethyl benzoylphosphonate but, significantly only when an excess of anhydride is used, *i.e.*, with the reverse of our conditions, and then only in low yield. We have confirmed this. The absence of the benzoylphosphonate

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[13] Kamai and Kukhtin, *Zhur. obshchei Khim.*, 1957, **27**, 949.

when excess of phosphite is used is now explicable on the above rationalisation. (*b*) It has been shown in this investigation that benzoic anhydride and diethyl benzoylphosphonate separately react with an excess of triethyl phosphite in chloroform to give the hexaethyl ester (VIII) and, further, it has been qualitatively observed that the reaction with diethyl benzoylphosphonate is faster than that involving benzoic anhydride. The absence of the intermediate (VII) is in accord with the increasing electrophilicity of the carbon atom next to the phenyl group which follows from an increase in the number of attached phosphonate groups. These reactions occurred on prolonged heating of the reaction mixture. Reaction for 30 min. gave an almost quantitative recovery of benzoic anhydride and triethyl phosphate, thus parallelling the corresponding reactions in carbon tetrachloride and in ether. The reaction carried out in carbon tetrachloride is complicated by the fact that triethyl phosphite and carbon tetrachloride react slowly to give diethyl trichloromethylphosphonate both in the dark and in ultraviolet light. The latter reaction is homolytic, and so probably is the former, the mechanism of which is now under investigation.

EXPERIMENTAL

Gas–Liquid Chromatography.—Analyses were carried out with the following instruments: (*a*) a Pye " Argon " chromatograph, with argon as carrier gas and 4-ft. APL and PEGA columns. The APL column was packed with Apiezon L on Celite 545, and the PEGA column with poly(ethylene glycol adipate) on Celite 545; (*b*) a Perkin-Elmer " Fraktometer," model 116, with nitrogen as carrier gas and a 2-metre column packed with Silicone oil (DC 200) on Celite 545.

Reagents.—Triethyl phosphite, fractionally distilled under nitrogen from sodium, had b. p. 60°/15 mm.; carbon tetrachloride had b. p. 76°; bromotrichloromethane had b. p. 105°; chloroform free from ethanol, had b. p. 61°; methylene dibromide had b. p. 98°.

Diethyl trichloromethylphosphonate [8] had b. p. 128°/14 mm., n_D^{20} 1·4620. Diethyl dichloromethylphosphonate, b. p. 82°/0·2, n_D^{25} 1·4513 (Found: C, 27·4; H, 4·8. Calc. for $C_5H_{11}Cl_2O_3P$: C, 27·2; H, 5·0%), was prepared as described by Bunyan and Cadogan.[9]

Benzoyl diethyl phosphate, b. p. 128—140°/0·1 mm., n_D^{25} 1·4847, was prepared in 30% yield by the reaction of triethyl phosphate (2 mol.), benzoyl chloride (1 mol.), and triethylamine (0·01 mol.) at 140—145° for 7 hr. Whetstone [14] reported b. p. 130—149°/1—2 mm., n_D^{20} 1·5000.

Diethyl benzoylphosphonate was prepared in 77% yield by the addition of triethyl phosphite (16·6 g., 1 mol.) to benzoyl chloride (14·0 g., 1 mol.) at 0° during 45 min. After addition of a further 3 mol. at 0° and 2 hr. at 100° the product was distilled (b. p. 105—108°/0·1 mm., n_D^{25} 1·5068). Kabachnik and Rossiiskaya [15] reported b. p. 141°/2·5 mm., n_D^{20} 1·5065. The 2,4-dinitrophenylhydrazone was prepared as described below.

Diethyl phenylphosphonate. Phenylphosphonic dichloride (b. p. 128—130°/10 mm.; 19·5 g.) in dry ether (50 ml.) was added dropwise to a solution from sodium (4·6 g.) in ethanol (100 ml.), and the mixture was boiled under reflux for 2 hr. The colloidal precipitate was coagulated by the addition of water (2 ml.), followed by ether (200 ml.). After filtration, the filtrate was washed with water (50 ml.), dried ($MgSO_4$), and distilled, to give diethyl phenylphosphonate (13·6 g., 63%), b. p. 90—95°/0·1 mm., n_D^{20} 1·4970 (Found: C, 56·2; H, 7·1. Calc. for $C_{10}H_{15}O_3P$: C, 56·1; H, 7·1%). Kosolapoff and Huber [16] reported b. p. 117—118°/1·5 mm., n_D^{25} 1·4935.

Dibenzoyl peroxide had m. p. 105·5° (decomp.). Di-*p*-chlorobenzoyl peroxide, m. p. 141° (lit.,[17] m. p. 140—141°), and di-*p*-bromobenzoyl peroxide, m. p. 148° (lit.,[17] m. p. 151—152°), were prepared by standard methods. Benzoyl *p*-nitrobenzoyl peroxide, m. p. 114° (lit.,[18] m. p. 113—114°), was prepared as described by Cadogan.[19]

p-Chlorobenzoic anhydride, m. p. 194° (lit.,[5] m. p. 191°), *p*-bromobenzoic anhydride, m. p. 219—220° (lit.,[20] m. p. 219—219·5°), and benzoic *p*-nitrobenzoic anhydride, m. p. 126—127°

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[14] Whetstone, U.S.P. 2,648,696.

[15] Kabachnik and Rossiiskaya, *Bull. Acad. Sci. U.R.S.S., Classe Sci. chim.*, 1945, 364; *Chem. Abs.*, 1946, **40**, 4688.

[16] Kosolapoff and Huber, *J. Amer. Chem. Soc.*, 1947, **69**, 2020.

[17] Swain, Stockmayer, and Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

[18] Cooper, *J.*, 1951, 3106.

[19] Cadogan, *J.*, 1959, 2844.

[20] Robertson and Neish, *Canad. J. Res.*, 1948, **26** *B*, 737.

(lit.,[5] m. p. 129—130°) (Found: C, 61·6; H, 3·4. Calc. for $C_{14}H_9NO_5$: C, 62·0; H, 3·4%), were prepared by standard methods.

Reactions of Diaroyl Peroxides with Triethyl Phosphite.—(i) *Di-*p*-chlorobenzoyl peroxide.* The peroxide (0·5 g.) was added portionwise in 10 min. to triethyl phosphite (2·0 g., 7·4 mol.). A vigorous reaction with evolution of white fumes occurred after 1 min. Light petroleum (b. p. 60—80°; 20 ml.) was added, the mixture was boiled for 5 min., and the *p*-chlorobenzoic anhydride (0·41 g., 81%; m. p. and mixed m. p. 194°) which separated was collected.

(ii) *Di-*p*-bromobenzoyl peroxide.* The peroxide (0·5 g.), on reaction with triethyl phosphite (2·0 g., 9·5 mol.) as described above, gave *p*-bromobenzoic anhydride (0·36 g., 75%; m. p. and mixed m. p. 219—220°).

(iii) *Benzoyl* p*-nitrobenzoyl peroxide.* The peroxide (0·75 g.), on reaction with the phosphite (2·0 g.) as described above, gave a semisolid product. Gas–liquid chromatography indicated the presence of eight components.

(iv) *Dibenzoyl peroxide.* (*a*) The peroxide (2·42 g., 1 mol.), on reaction with triethyl phosphite (1·66 g., 1 mol.) as described above, gave a brown liquid which on chromatography on silica and elution with 1 : 2 v/v ether–light petroleum (b. p. 60—80°) gave benzoic anhydride (2·00 g., 90%; m. p. 34—35°, mixed m. p. 36—37°). Elution with chloroform–ethanol (1 : 1) gave triethyl phosphate (1·20 g., 66%).

(*b*) In a similar experiment, the peroxide (1·0 g.) was added in one portion to triethyl phosphite (3·32 g., 4·8 mol.). An almost explosive reaction occurred after 1½ min. Gas–liquid chromatography of the mixture (column APL at 200°) indicated the presence of *ca.* 1% of diethyl phenylphosphonate. This was confirmed by the use of the PEGA column at 200°.

(*c*) Dibenzoyl peroxide (1·0 g.) was added in very small portions to triethyl phosphite (1·0 g.) in 1 hr. at 0°. There was no evolution of heat. After 15 hr. at 0°, gas–liquid chromatography (column APL at 200°) indicated the absence of diethyl phenylphosphonate. Distillation and chromatography on silica gave benzoic anhydride (0·62 g., 70%), m. p. and mixed m. p. 39—40°.

Reactions of Diaroyl Peroxides with Triethyl Phosphite in Solvents.—Triethyl phosphate, isolated from products of the following experiments, had b. p. 30—40°/0·1 mm., n_D^{25} 1·4030—1·4050, and the correct infrared spectrum.

(i) *Di-*p*-bromobenzoyl peroxide in ether.* Triethyl phosphite (1·24 g.) in dry ether (15 ml.) was added to a suspension of di-*p*-bromobenzoyl peroxide (3·0 g., 1 mol.) in boiling ether (40 ml.), and the mixture was boiled under reflux under nitrogen for 1½ hr. The product was filtered and the residue (2·79 g., m. p. 216°) on recrystallisation from benzene gave *p*-bromobenzoic anhydride (2·53 g., 96%), m. p. and mixed m. p. 219—220°. The filtrate, on distillation, gave triethyl phosphate (1·28 g., 96%) and left a residue (0·14 g.).

(ii) *Di-*p*-chlorobenzoyl peroxide in ether.* Reaction of the peroxide (1·0 g.) with triethyl phosphite (0·54 g., 1 mol.) in dry ether (50 ml.), as described for the previous experiment, gave *p*-chlorobenzoic anhydride (0·58 g., 90%), m. p. and mixed m. p. 194—195°, triethyl phosphate (0·57 g., 98%), and a residue (0·03 g.).

(iii) *Benzoyl* p*-nitrobenzoyl peroxide in ether.* Triethyl phosphite (1·0 g.) in ether (20 ml.) was added to a suspension of the peroxide (1·6 g., 1 mol.) in ether (100 ml.), and the mixture was stirred at 15° overnight under nitrogen. The peroxide dissolved after 30 min. and later a crystalline deposit was formed. Light petroleum (b. p. 60—80°) was added and the precipitate (m. p. 120—121°) was filtered off. Recrystallisation from acetone–light petroleum (b. p. 60—80°) gave benzoic *p*-nitrobenzoic anhydride (1·37 g., 85%; mixed m. p. 127°; correct infrared spectrum) (Found: C, 61·8; H, 3·2. Calc. for $C_{14}H_9NO_5$: C, 62·0; H, 3·3%). The filtrate, on distillation, gave triethyl phosphate (0·80 g., 73%).

A replicate reaction carried out for 20 min. at the b. p. gave identical results. Neither *p*-nitrobenzoic nor benzoic anhydride was present, as demonstrated by chromatography on silica gel which separates these compounds, and it was shown that they were not transformed into the mixed anhydride under the conditions of the experiment.

(iv) *Dibenzoyl peroxide in ether.* The phosphite (1·66 g., 1 mol.) and the peroxide (2·42 g., 1 mol.) were allowed to react in ether (50 ml.) as described in experiment (i). Distillation gave triethyl phosphate (1·77 g., 97%) and a fraction, b. p. 120—138°/0·1 mm., n_D^{20} 1·5730 (2·15 g.), which on chromatography on silica gel with 1 : 2 ether–light petroleum (b. p. 60—80°) as eluant gave benzoic anhydride (1·83 g., 81%), m. p. and mixed m. p. 36—39°.

(v) *Dibenzoyl peroxide in carbon tetrachloride.* Triethyl phosphite (1·66 g., 1 mol.) was added to the peroxide (2·42 g., 1 mol.) in carbon tetrachloride (12·32 g., 8 mol.). A vigorous reaction occurred after 1 min. After 10 min., distillation gave triethyl phosphate (1·77 g., 97%), benzoic anhydride (2·21 g., 99%), b. p. 124—130°/0·1 mm., m. p. 36—37°, mixed m. p. 37—38°, and a residue (0·09 g.).

(vi) *Dibenzoyl peroxide in chloroform.* Reaction of triethyl phosphite (1·66 g., 1 mol.) and dibenzoyl peroxide (2·42 g., 1 mol.) in chloroform (9·6 g., 8 mol.), as described for experiment (v), gave triethyl phosphate (1·76 g., 96%) and benzoic anhydride (2·14 g., 94%).

No reaction occurred between the phosphite and chloroform (4 equiv.) after 18 hr. at the b. p. The addition of dibenzoyl peroxide (0·025 mole per mole of phosphite) and heating for 18 hr. at 85° gave triethyl phosphate (9%), but reaction at 110° for 42 hr. with 0·05 mole of dibenzoyl peroxide per mole of phosphite gave an approximately equimolar mixture of triethyl phosphate and ethyl benzoate (12%) and a high-boiling residue (6%).

(vii) *Prolonged reaction of dibenzoyl peroxide in chloroform.* Triethyl phosphite (3·32 g., 0·02 mol.), chloroform (9·6 g., 0·08 mol.), and dibenzoyl peroxide (1·936 g., 0·008 mol.) were boiled under nitrogen for 48 hr. The excess of chloroform was removed to give a yellow residue (4·36 g.) which, in a replicate experiment, was shown by gas-liquid chromatography not to contain diethyl trichloromethylphosphonate or dichloromethylphosphonate. Distillation of a portion (3·79 g.) gave (i) a colourless oil, b. p. 38—40°/0·04 mm. (1·953 g.), which was shown in a replicate experiment to consist of triethyl phosphate and ethyl benzoate by gas–liquid chromatography, (ii) an oil, b. p. 120—144°/0·03 mm. (1·628 g.), and (iii) a residual colourless solid (0·18 g.). A portion (1·241 g.) of fraction (ii) was chromatographed on silica. Elution with 1 : 2 ether–light petroleum (500 ml.) gave benzoic anhydride (0·24 g., 22·4% based on peroxide), m. p. and mixed m. p. 40°. Elution with ethanol gave an oil (1·01 g.), b. p. 144—146°/0·01 mm., n_D^{24} 1·4780, which did not contain chlorine. This is formulated as hexaethyl benzylidynetriphosphonate by comparison with an authentic specimen prepared as described below. The yield was 40%, based on peroxide.

Reaction of Triethyl Phosphite with Diethyl benzoylphosphonate.—The phosphite (9·96 g., 4 mol.) and diethyl benzoylphosphonate (3·63 g., 1 mol.) were boiled under reflux in chloroform (28·8 g., 16 mol.) under nitrogen for 66 hr. Distillation gave, after removal of unchanged material, *hexaethyl benzylidynetriphosphonate* (2·51 g., 32%), b. p. 142—160°/0·05 mm., n_D^{26} 1·4850, with an infrared spectrum identical with material obtained from the previous experiment (Found: C, 45·7; H, 6·7. $C_{19}H_{35}O_9P_3$ requires C, 45·6; H, 7·0%).

Reactions of Triethyl Phosphite with Benzoic Anhydride.—(i) *With an excess of triethyl phosphite.* The phosphite (6·64 g., 4 mol.) and benzoic anhydride (2·26 g., 1 mol.) were boiled under reflux in chloroform (19·2 g., 16 mol.) under nitrogen for 65 hr. Distillation gave triethyl phosphite (5·0 g.), b. p. 62°/10 mm., impure ethyl benzoate (0·9 g.), b. p. 96—98°/10 mm., and an oil (2·41 g.), b. p. 120—156°/0·1 mm. Chromatography of the last fraction on silica as described above gave benzoic anhydride (1·30 g.) and hexaethyl benzylidenetriphosphonate (0·75 g., 0·55 mol.), b. p. 140—150°/0·1 mm. (0·55 g.), identical with samples prepared in previous experiments.

(ii) *With excess of benzoic anhydride.* Triethyl phosphite (3·32 g., 1 mol.) and benzoic anhydride (13·56 g., 3 mol.) were allowed to react in chloroform (19·2 g., 8 mol.) as described above. Distillation gave impure ethyl benzoate (2·05 g.), b. p. 35—40°/0·05 mm., and an oil (13·18 g.), b. p. 110—135°/0·1 mm., and left a residue (1·10 g.). Chromatography on silica gave benzoic anhydride (11·27 g., 83%) and an oil (1·59 g.), b. p. 120—145°/0·1 mm., which contained diethyl benzoylphosphonate (infrared spectrum). Its crude 2,4-dinitrophenylhydrazone was separated from benzoic anhydride by chromatography on kieselguhr–bentonite, followed by alumina. The product had m. p. 172—174° on recrystallisation from ethanol, and 171—173° on admixture with authentic diethyl benzoylphosphonate 2,4-dinitrophenylhydrazone (Found: C, 48·8; H, 4·9. Calc. for $C_{17}H_{19}N_4O_7P$: C, 48·4; H, 4·5%) (lit.,[21] m. p. 171—172°).

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