

PHOTOLYSIS OF ACYLPHOSPHINE OXIDES II: THE INFLUENCE OF METHYL SUBSTITUTION IN BENZOYLDIPHENYLPHOSPHINE OXIDES

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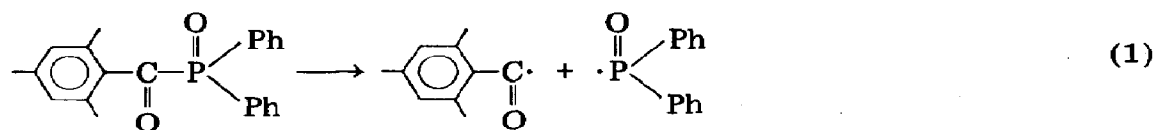
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Summary

Argon-saturated dilute solutions of 2-methyl-, 4-methyl-, 2,4,6-trimethyl- and non-substituted benzoyldiphenylphosphine oxide (OTDPO, PTDPO, TMDPO and BDPO respectively) in various solvents were irradiated with flashes (duration, 20 ns) of 347 nm light. All compounds underwent α scission in times much shorter than the flash time: $\phi(\alpha) = 0.5 - 0.6$ (OTDPO, TMDPO and BDPO) and $\phi(\alpha) = 1.0$ (PTDPO). Diphenylphosphonyl radicals generated in this way characteristically absorb light around 330 nm. In the case of OTDPO, photoenolization competes with α scission, and transient spectra were observed which were assigned to the excited triplet ($k = 3 \times 10^7$ s⁻¹) and to the ground state ($k = (3 \times 10^5) - (1.5 \times 10^4)$ s⁻¹) of the enols. TMDPO did not undergo enolization. It is concluded that enolization involves triplets and that a triplet lifetime longer than a few nanoseconds is a prerequisite for its occurrence.

1. Introduction

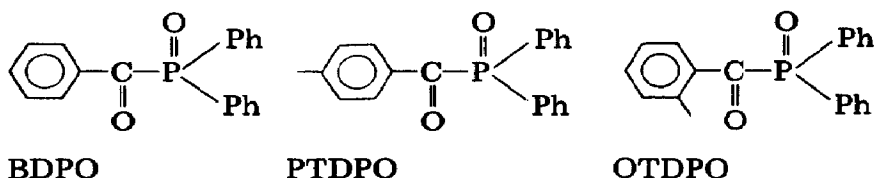
In Part I of this series of papers [1] we reported that in dilute solution 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) undergoes α scission according to the following reaction upon irradiation with light of wavelength $\lambda = 347$ nm.



TMDPO

(Ph \equiv phenyl)

The quantum yield of this process was determined as $\phi(\alpha) = 0.5 - 0.6$. Diphenylphosphonyl radicals $(\text{Ph})_2\dot{\text{P}}=\text{O}$ generated by reaction (1) were found [2] to absorb strongly at about 330 nm ($\epsilon = 1.9 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). In the present paper, experiments with three compounds similar to TMDPO but differing in the number of hydrogens substituted by methyl groups at the benzoyl group will be described: benzoyldiphenylphosphine oxide (BDPO), 4-methylbenzoyldiphenylphosphine oxide (PTDPO) and 2-methylbenzoyldiphenylphosphine oxide (OTDPO)



2. Experimental details

2.1. Materials

BDPO, PTDPO, OTDPO and TMDPO were synthesized as described previously [3]. Dichloromethane, methanol, ethanol and cyclohexane, all of Uvasol quality, and hexamethylphosphonic acid triamide (purity, 99.3%) were obtained from E. Merck. They were used without further purification. *trans*-Piperylene (*trans*-1,3-pentadiene; purity, 99%) was obtained from EGA and used as received.

2.2. Irradiations

Dilute solutions of phosphine oxides, in most cases made free from oxygen by bubbling with purified argon, were irradiated in rectangular quartz cells. The irradiations were carried out at 347 nm with a ruby laser operated in conjunction with a frequency doubler. The flash duration was about 20 ns.

Actinometry was performed with solutions of benzophenone ($1.15 \times 10^{-3} \text{ M}$) containing naphthalene ($1.03 \times 10^{-1} \text{ M}$). The absorbed dose per flash was calculated from the concentration of naphthalene triplets formed by energy transfer from benzophenone with $\epsilon_{\text{T-T}} = 1.32 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 425 nm and $\phi(\text{T}) = 1.0$. The maximum laser output at $\lambda = 347 \text{ nm}$ was 5×10^{16} photons per flash, corresponding to an absorbed dose D_{abs} per flash of $3.6 \times 10^{-5} \text{ einstein l}^{-1}$ at an optical density (OD) of 0.1.

3. Results

3.1. Emission measurements

Figure 1 shows absorption and emission spectra recorded with the four phosphine oxides in dichloromethane or cyclohexane solution. The

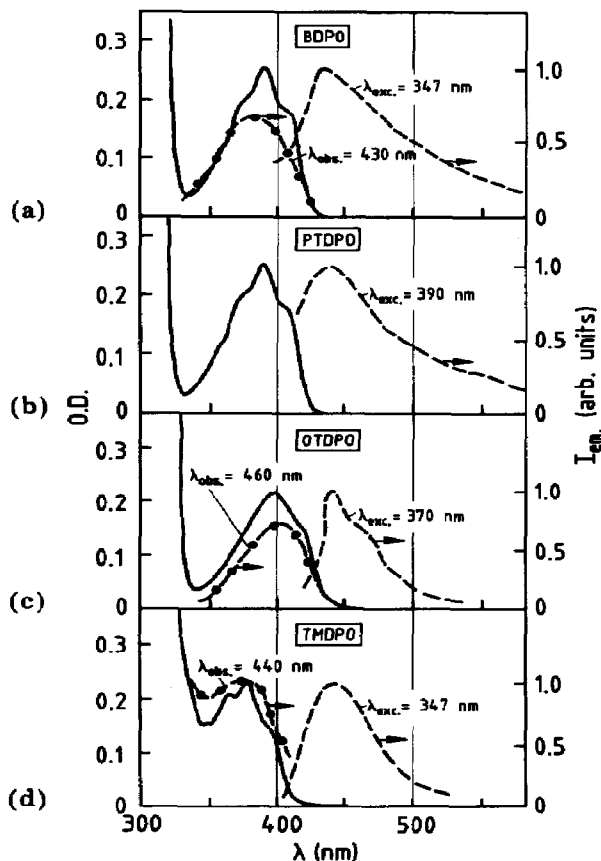


Fig. 1. Ground state absorption and emission spectra of benzoyldiphenylphosphine oxides recorded at room temperature: —, absorption spectra; ---, emission spectra; - · -, excitation spectra. [BDPO] = 3.7×10^{-3} M; [PTDPO] = 1.3×10^{-3} M; [OTDPO] = 7.3×10^{-4} M; [TMDPO] = 4.0×10^{-4} M; CH_2Cl_2 was the solvent for (a), (b) and (d) and cyclohexane was the solvent for (c).

emission spectra possess maxima around 440 nm. Apart from PTDPO where the emission was very weak, excitation spectra were recorded which strongly resembled the absorption spectra. Therefore, it was concluded that the emission band corresponds to the ground state absorption band due to the $S_0 \rightarrow S_1$ transition. From the intersection of the two spectra at about 415 nm the singlet energy (0-0 transition) of the phosphine oxides was estimated as about 290 kJ mol^{-1} .

Because of the very weak emission intensity, the single-photon counting technique could only be employed for lifetime measurements in the case of TMDPO, where the emission intensity was found to decay exponentially with $\tau \approx 0.3 \text{ ns}$ [1].

3.2. Absorption measurements with BDPO, TMDPO and PTDPO

Upon irradiation of the phosphine oxides in dilute solution with flashes (duration, 20 ns; $\lambda_{\text{inc}} = 347 \text{ nm}$) transient difference spectra in the

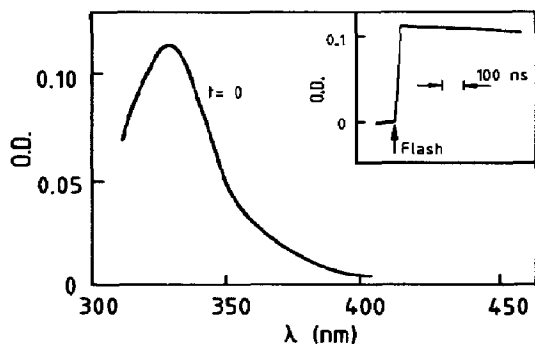


Fig. 2. Transient difference absorption spectrum formed during the flash ($\lambda_{\text{inc}} = 347 \text{ nm}$). PTDPO in argon-saturated CH_2Cl_2 solution ($7.6 \times 10^{-4} \text{ M}$). $D_{\text{abs}} = 3.0 \times 10^{-5} \text{ einstein l}^{-1}$. (Inset, oscillogram depicting the increase in the OD during the flash; flash duration, about 20 ns.) Similar spectra were recorded with BDPO and TMDPO.

wavelength range between 300 and 450 nm were observed. In the cases of BDPO and PTDPO the transient spectrum with $\lambda_{\text{max}} = 335 \text{ nm}$ shown in Fig. 2 was recorded at the end of the flash. It strongly resembles the spectrum observed with TMDPO [1] and was therefore assigned to phosphonyl radicals $(\text{Ph})_2\dot{\text{P}}=\text{O}$. O_2 did not affect the formation of the transient absorption but strongly accelerated its decay. The latter process followed pseudo-first-order kinetics yielding a rate constant of $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction $(\text{Ph})_2\dot{\text{P}}=\text{O} + \text{O}_2$. In the absence of O_2 the decrease in the transient absorption followed second-order kinetics with $\tau_{1/2}^{-1}$ increasing linearly with the OD measured at the end of the flash. This result is expected on the basis of the equation

$$\tau_{1/2}^{-1} = 2k_{\text{R}}[\text{R}\cdot]_0 \quad (2)$$

by taking into account that $\text{OD}_0 \propto [\text{R}\cdot]_0$. Here, $\text{R}\cdot$ denotes phosphonyl radicals which undergo self-reactions according to reaction (3) in the absence of any other reactant.



The results obtained with BDPO and TMPO led us to the same conclusion as that arrived at previously [1] in the case of TMDPO, namely that reaction (3) is an encounter-controlled process with $2k_{\text{R}} = (3.6 \times 10^9) - (7.2 \times 10^9) \text{ M}^{-1} \text{ s}^{-1}$.

As has been reported previously [1], naphthalene quenching experiments permitted an estimate to be made for the triplet lifetime of TMDPO of about 0.3 ns. In order to detect energy transfer via the formation of the characteristic T-T absorption of naphthalene at about 420 nm, high quencher concentrations had to be employed, *i.e.* $[\text{naphthalene}] > 0.5 \text{ M}$. It was not reported in the previous paper [1] that under these conditions another reaction also occurred, as could be concluded from the formation of a new absorption band at about 360 nm. The oscillograms shown in Fig. 3

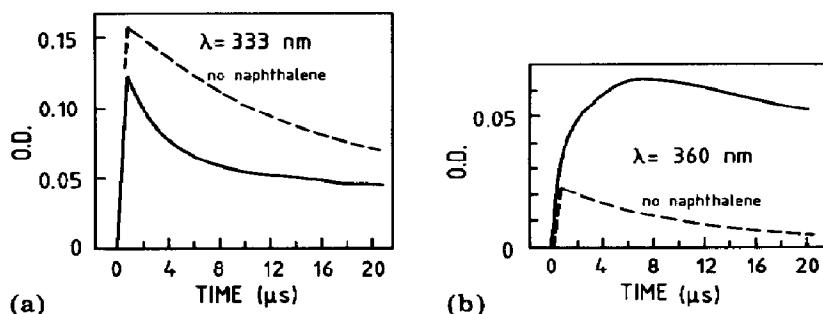
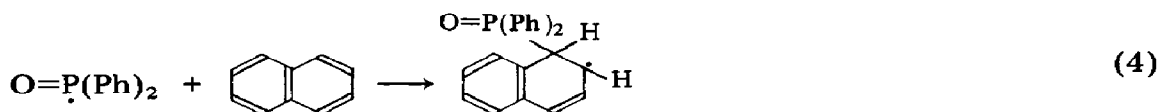


Fig. 3. Flash photolysis of TMDPO in argon-saturated benzene solution (4.2×10^{-4} M) in the presence and absence of naphthalene (1 M) ($D_{\text{abs}} = 1.85 \times 10^{-5}$ einstein l^{-1}): oscillograms depicting changes in the OD at (a) 333 nm and (b) 360 nm, during and after the flash.

illustrate how this absorption grew in while the decrease in the absorption at 333 nm simultaneously was accelerated. It appears very probable that we were observing the addition of phosphonyl radicals to naphthalene according to the reaction



Analogous adduct formations involving diethoxyphosphonyl radicals ($\text{O}=\dot{\text{P}}(\text{OEt})_2$) have been investigated by Jason and Fields [4]. Upon applying a pseudo-first-order kinetic treatment, the rate constant of reaction (4) was evaluated as $k = 5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

3.3. Absorption measurements with OTDPO

Upon irradiation of OTDPO in dilute solution a transient spectrum possessing two maxima, at 330 nm and at 395 nm, was observed at the end of the flash as can be seen from Fig. 4. The inset of Fig. 4 shows that immediately after the flash the OD at 330 nm rapidly decreased with $\tau_{1/2} \approx 20$ ns while the OD at 395 nm increased simultaneously. The remaining absorption spectrum exhibited wavelength-dependent decay kinetics. In the absence of O_2 the major part of the OD at 330 nm decreased according to second-order kinetics, which is analogous to the decay behaviour of the absorption of phosphonyl radicals observed with the other three phosphine oxides.

The decay of the absorption band around 395 nm occurred according to first-order kinetics. The lifetimes recorded in different solvents (compiled in Table 1) were independent of the absorbed dose per flash, *i.e.* were independent of the initial concentration of the species under investigation. O_2 did not influence the decay kinetics. Also, piperylene at concentrations up to 0.1 M did not affect the decay rate; however, it strongly accelerated

TABLE 1

Irradiation of OTDPO in solutions of different solvents: lifetime of the transient absorption at 395 nm

Solvent	τ (μ s)
Benzene (argon-saturated)	5.4
Benzene (air)	5.2
Ethanol (argon-saturated)	10.1
Ethanol (argon-saturated; 0.1 M piperylene)	9.6
Hexamethylphosphoric acid triamide	50

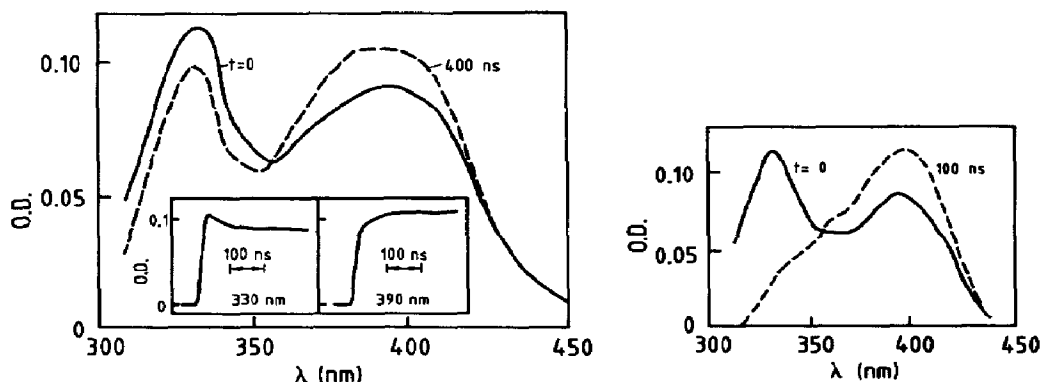


Fig. 4. Transient difference absorption spectra recorded with OTDPO in argon-saturated ethanolic solution (7.5×10^{-4} M) at the end of the flash and 400 ns after the flash (duration, 20 ns). $D_{\text{abs}} = 4.7 \times 10^{-5}$ einstein l^{-1} ; $\lambda_{\text{inc}} = 347$ nm. (Inset, oscillograms depicting changes in the OD at 330 and 390 nm.)

Fig. 5. Transient difference absorption spectra recorded with OTDPO in argon-saturated ethanolic solution (7.5×10^{-4} M) containing *trans*-piperylene (0.1 M), at the end of the flash and 100 ns after the flash. $D_{\text{abs}} = 4.7 \times 10^{-5}$ einstein l^{-1} ; $\lambda_{\text{inc}} = 347$ nm; flash length, about 20 ns.

the decrease in the absorption at 330 nm. This is illustrated in Fig. 5 where the spectra recorded at the end of the flash and 100 ns later are shown. The absorption of the phosphoryl radicals disappeared completely within 100 ns, whereas simultaneously the absorption band at 395 nm significantly increased. The decrease in the absorption at both 330 nm and 395 nm is illustrated by the two oscilloscope traces shown in Fig. 6. From the dependence of the decay rate of the OD at 330 nm on the piperylene concentration, the rate constant of the reaction of diphenylphosphonyl radicals with piperylene was determined as 1.6×10^8 $M^{-1} s^{-1}$.

As will be explained in more detail in Section 4, the long-lived absorption band at 395 nm is attributed to ground state enol molecules formed by interaction of excited carbonyl groups with the hydrogens of the methyl group in the ortho position. The absorption band at 330 nm is assigned to phosphoryl radicals whereas the short-lived absorption changes depicted in the inset of Fig. 4 indicate the existence of a precursor (probably a triplet).

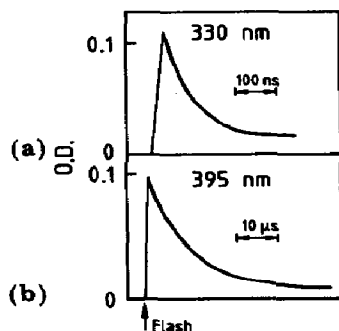


Fig. 6. Photolysis of OTDPO in ethanolic solution with the same conditions as those described in the caption to Fig. 5. The oscilloscope traces depict the changes in the OD at (a) 330 nm and (b) 395 nm during and after the flash.

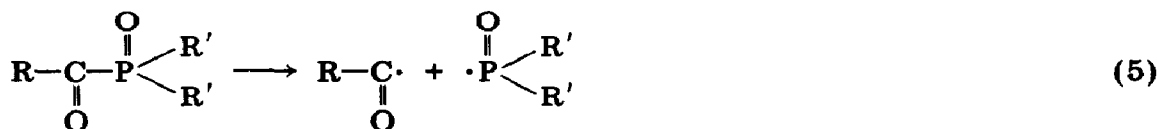
TABLE 2

Quantum yields of α scission determined in argon-saturated CH_2Cl_2 solutions

Compound	$\text{OD}_{331 \text{ nm}}/D_{\text{abs}}$ (1 einstein^{-1})	$\phi(\alpha)$
BDPO	8.0×10^3	0.5
OTDPO	9.6×10^3	0.6
PTDPO	16.5×10^3	1.0
TMDPO	9.7×10^3	0.6

3.4. Quantum yields of α scission

By comparing the extent of the transient absorption due to phosphonyl radicals at 331 nm the quantum yields of α scission according to reaction (5) were estimated.

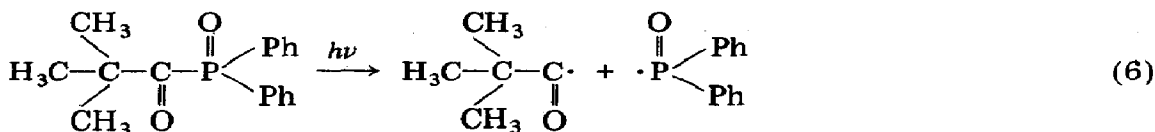


The dose-normalized ODs and the quantum yields relative to that found previously for TMDPO [1] are given in Table 2. Obviously, all four compounds undergo α scission quite readily. The highest quantum yield was observed in the case of the 4-methyl-substituted compound (PTDPO). The 2-methyl-substituted and the 2,4,6-trimethyl-substituted compounds (OTDPO and TMDPO respectively) definitely exhibited a weaker ability to undergo α cleavage, equal to that of the non-substituted compound (BPDO). At present, it cannot be explained why PTDPO exhibits a behaviour different from that of the other three compounds.

4. Discussion

Upon irradiation of the four benzoyldiphenylphosphonyl oxides studied in this work a very strong transient absorption band around 330 nm was observed which was attributed to diphenylphosphonyl radicals. At first, it appeared feasible to attribute this band to ketone triplets, because triplets of acetophenone and related compounds absorb light relatively strongly in this wavelength range [5, 6]; however, this possibility was ruled out on the basis of the experimental findings which led to the conclusion that the 330 nm band is attributable to diphenylphosphonyl radicals. The reasoning leading to this conclusion is as follows.

(1) Upon flash photolysis of pivaloyldiphenylphosphine oxide (PDPO) the same transient absorption band ($\lambda_{\text{max}} \approx 330$ nm) was observed as in the cases of BDPO, OTDPO, PTDPO and TMDPO [1]. PDPO undergoes α scission quite readily:



At 330 nm, triplets of PDPO are expected to absorb light very weakly, if at all, on taking into account that triplets of aliphatic carbonyl compounds generally absorb light much more weakly than those of aromatic carbonyl compounds.

(2) Naphthalene reduced the OD at 330 nm formed during the 20 ns flash and the T-T absorption characteristic of naphthalene triplets at about 420 nm was generated *during* the flash. If the absorption band at 330 nm were due to ketone triplets which can be quenched by naphthalene, its lifetime (which amounts to several microseconds) should correlate with that for the formation of the naphthalene T-T absorption. Actually, the lifetime of ketone triplets was estimated as 0.3 ns on the basis of the dependence of the OD at 420 nm on the naphthalene concentration. The fact that the decay rate of the OD at 330 nm was accelerated by naphthalene can be explained by the addition reaction of diphenylphosphonyl radicals to naphthalene according to reaction (4). In the present work, the occurrence of this reaction was indicated by the absorption at 360 nm which grew in with the same rate as that of the decrease in the OD at 330 nm (see Fig. 3(b)).

(3) Apart from the results obtained with OTDPO, which will be considered below, the OD at 330 nm, which had formed during the flash, decayed according to second-order kinetics, the first half-life of the decay being proportional to the reciprocal absorbed dose, *i.e.* to the initial OD. This behaviour is in accordance with the assignment of the 330 nm band to phosphonyl radicals. Actually, second-order kinetics could also be indicative of T-T annihilation; however, for this the OD would be expected to

decrease according to two modes of decay: an initial second-order mode and a subsequent first-order mode, the proportions of each being strongly dependent on the absorbed dose per flash. With BDPO, PTDPPO and TMDPO, however, only one mode of decay was observed and this followed second-order kinetics.

In the case of OTDPO, two modes of decay of the OD at 330 nm were found: an initial first-order mode followed by a second-order mode. The former is presumably due to triplets, whereas the latter is assigned to diphenylphosphonyl radicals in accordance with the assignment made in the cases of the other three phosphine oxides. The accelerating effect of *trans*-piperylene on the rate of decay of the OD at 330 nm (see Figs. 5 and 6) is attributed to this compound reacting quite efficiently with diphenylphosphonyl radicals, which were found also to possess a high reactivity towards other unsaturated compounds [1, 7].

On the basis of the assignment of the transient absorption band at 330 nm to diphenylphosphonyl radicals, the results of this work indicate that the four benzoyldiphenylphosphine oxides under investigation undergo α cleavage quite readily. The substitution of hydrogens at the benzoyl group by methyl groups only has a drastic effect in the case of para substitution, as can be seen from Table 2. PTDPPO is cleaved twice as effectively as the non-substituted phosphine oxide BPDO. The trimethyl-substituted compound TMDPO undergoes α scission with the same yield as the non-substituted compound indicating that the three methyl groups do not exert any influence on α scission.

In the case of the ortho-substituted compound, interaction of the methyl group with the excited carbonyl group strongly competes with α scission. It is assumed that this interaction leads to the formation of enols, as is illustrated in Fig. 7.

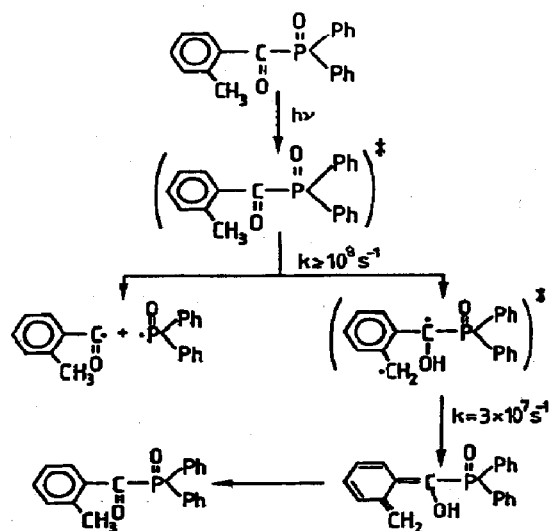
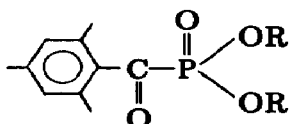


Fig. 7. Photolysis of *o*-methylbenzoyldiphenylphosphine oxide.

As for the photoenolizations observed with other compounds [6, 8 - 14] it is assumed that in the present case the short-lived transient ($\tau_{1/2} \approx 20$ ns; see Fig. 4, inset) is due to the enol triplet which is converted to the ground state enol with $k = 3 \times 10^7$ s⁻¹. The deactivation of enol triplets should lead to *Z* and *E* isomers which should be distinguishable by their different lifetimes. In this case the decay of the OD at 390 nm would be expected to occur according to two modes. Only one mode was detected, however, which is assigned to the *E* isomer in accordance with the fact that the lifetime is strongly solvent dependent (see Table 1). The *Z* isomer, however, might be rather short-lived, having a lifetime similar to that of the enol triplet. Therefore, they might not be detectable on using the technique employed in this work.

It is notable that photoenolization was not observed with TMDPO, which also possesses methyl groups in the ortho position, whereas it was detected with trimethylbenzoylphosphonates of the structure [15]



(R \equiv CH₃ (TMDPM) or C₂H₅ (TMDPE))

The different behaviour might be correlated with the lifetime of the ketone triplets which is very short (0.3 ns) in the case of TMDPO and substantially longer (more than 3 ns) in the case of the phosphonates TMDPM and TMDPE. It seems, therefore, that interactions between methyl groups in the ortho position and carbonyl groups involve triplet states and that they only become important if intersystem crossing is significant and if ketone triplets live longer than a few nanoseconds.

The absence of photoenolization, in the case of TMDPO, may also be discussed in terms of its ground state conformation being unfavourable to interaction of the carbonyl group with an *ortho*-methyl group. It is pertinent to note that 2,4,6-trimethylphenylalkyl ketones are known to be highly twisted in their ground states [16]. Therefore, it can be assumed that in the present case also, substitution by a methyl group of a second hydrogen in the ortho position to the carbonyl produces a conformation with the carbonyl in a position almost perpendicular to the trimethylphenyl moiety. Thus, the interactions of the excited carbonyl with *ortho*-methyl groups are also strongly impeded. Evidence for this steric effect emerges from the ground state UV spectra (see Fig. 1) which show a slight blue shift of the n, π^* absorption in the case of TMDPO. From this reasoning it follows that, in contrast to dimethoxyphosphonyl and diethoxyphosphonyl groups, the diphenylphosphonyl group must exert a stabilizing effect on the conformation for which enolization is unfavourable, because TMDPM and TMDPE undergo enolization but TMDPO does not.

Acknowledgments

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