

## Electron Spin Resonance Studies on the Photodissociation of 2,4,6-Trimethylbenzoyldiphenylphosphine Oxide †

Mikiharu Kamachi\* and Keiji Kuwata

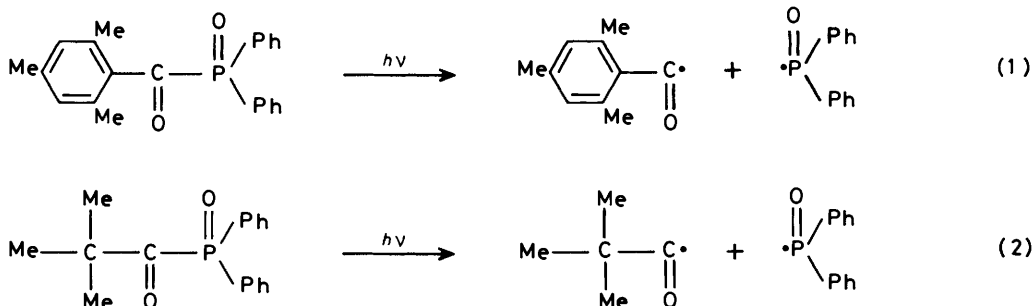
Faculty of Science, Osaka University, Toyonaka, Osaka, 560 Japan

Takashi Sumiyoshi and Wolfram Schnabel

Hahn-Meitner-Institut Berlin, Bereich Strahlen-chemie, D-1000 Berlin 39, Federal Republic of Germany

Upon irradiation of 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) with u.v. light in O<sub>2</sub>-free benzene solution a doublet indicative of phosphorus-centred radicals was observed. By this technique  $\alpha$ -scission of TMDPO yielding the diphenylphosphinoyl radical (Ph<sub>2</sub>P=O) was directly evidenced. This radical was found to add to the carbonyl groups of intact TMDPO with  $k = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  forming a radical of the general structure A[Ph<sub>2</sub>P(O)]COP(O)Ph<sub>2</sub> (A: 2,4,6-trimethylbenzoyl). In the time-resolved measurements CIDEP due to the radical-pair mechanism was observed.

Recent studies have led to the introduction of acylphosphine oxides and acylphosphonates as novel photoinitiators for photocuring of polymer resins.<sup>1</sup> 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TMDPO) especially proved suitable as a photoinitiator with respect to its applicability to industrial processes. In the laser flash photolysis of TMDPO a transient optical absorption spectrum with a maximum at *ca.* 330 nm was observed.<sup>2,3</sup> Since the same transient optical absorption spectrum was observed in the flash photolysis of pivaloyldiphenylphosphine oxide it was assigned to the diphenylphosphinoyl radical produced by the dissociation of the acylphosphine oxides according to reactions (1) and (2).



In these studies,<sup>2,3</sup> the 2,4,6-trimethylbenzoyl radical which is generated simultaneously with the diphenylphosphinoyl radical according to reaction (1) was not detected due to its comparatively weak absorptivity. It seemed, therefore, meaningful to obtain support for this mechanism from e.s.r. studies. Recently, one of us (K. K.<sup>4</sup>) developed a new instrument for time-resolved e.s.r. studies which was used in this work to study the mechanism of the photolysis of TMDPO. The results corroborate the assumption that TMDPO is photolysed very rapidly according to reaction (1). It should be pointed out that it was possible to follow changes in the e.s.r. spectra in the time-range of a few hundred ns.

### Experimental

**Materials.**—2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TMDPO) was obtained from BASF. Its synthesis has been described previously.<sup>1</sup> Benzene was purified as described elsewhere.<sup>5</sup>

**E.S.R. Measurements.**—Continuous irradiation with u.v. light. E.s.r. spectra were recorded while continuously irradiating

TMDPO in benzene solution (0.1M) at room temperature with the light of a 500 W high-pressure mercury lamp. Prior to irradiation the solutions were degassed by repetitive freezing, pumping and thawing. A JEOL JES-FE 1X spectrometer operated with a modulation of 100 kHz was used. Simulations of e.s.r. spectra were performed with the aid of a JEOL EC-6 computer. The *g*-factors were measured by the comparison method using DPPH.

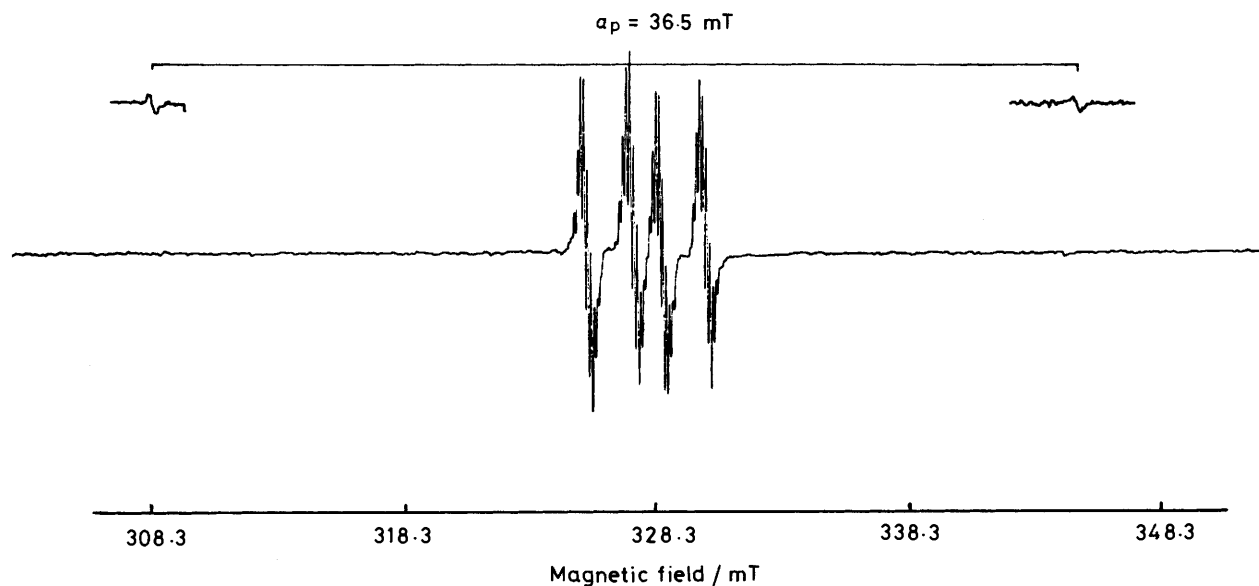
**Flash photolysis with 337.1 nm light.** Degassed benzene solutions were irradiated with 20 ns flashes of a nitrogen laser ( $\lambda_{\text{inc}} = 337.1 \text{ nm}$ ). Time-resolved e.s.r. measurements were carried out with an X-band instrument operated without

magnetic field modulation. Rise and decay of e.s.r. signals were recorded at a given range of the magnetic field. The signals were stored in a transient memory (Iwasaki DM 90) which was connected to a microcomputer. Three-dimensional spectra were plotted with the aid of a CRT display. Details of the e.s.r. spectrometer will be described elsewhere.<sup>4</sup> The *g*-factors were determined by the comparison method using DPPH.

### Results and Discussion

**Continuous Irradiations.**—A typical e.s.r. spectrum is shown in Figure 1. It consists of four lines exhibiting hyperfine splitting, located at about *g* 2.0035. When the sensitivity of the e.s.r. spectrometer was increased a weak doublet resonance with a hyperfine splitting constant of 36.5 mT was detected (Figure 1). Upon turning the photolysing light off, the weak doublet disappeared immediately whereas the multiplet lines decayed

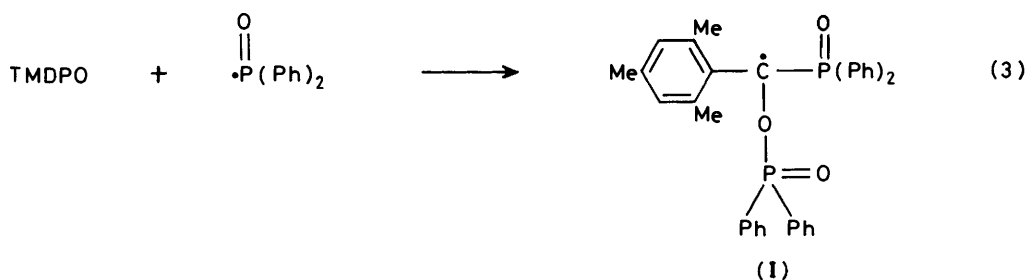
† This paper was presented at the XII International Conference on Photochemistry at Tokyo, August 1985.



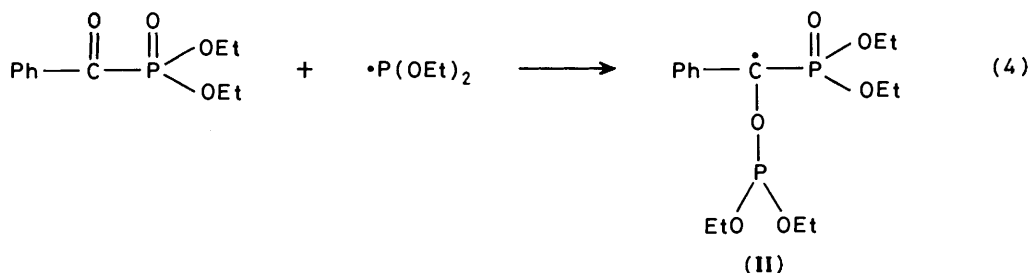
**Figure 1.** E.s.r. spectrum recorded at  $328 \pm 25$  mT during the continuous photolysis of TMDPO in degassed benzene solution (0.1M) at room temperature

more slowly. From this result it is inferred that there were two kinds of paramagnetic species in the system. The weak doublet is the signal from the diphenylphosphinoyl radical.<sup>6-8</sup> In order to obtain information on the origin of the strong four-line spectrum, measurements were carried out in a narrow range of magnetic field strength. The e.s.r. spectrum obtained is shown in Figure 2(a). It consists of a doublet of doublets located at  $g$  2.0035, each band split into 10 lines. The measured e.s.r. spectrum of radical (I) was computer-simulated with two phosphorus splitting values of  $a_p$  2.82 mT and  $a_p$  1.67 mT,<sup>9</sup> and  $a_H$  0.13 mT for the hyperfine interaction of the unpaired electron with the nine protons of the methyl groups in *ortho* and *para* positions. The simulated spectrum is shown in Figure 2(b). Accordingly, this spectrum is assigned to a carbon-centred radical formed by the reaction of diphenylphosphinoyl radicals with intact TMDPO.

**Flash Photolysis.**—In order to obtain information on the kinetics of the decay of the transient species, flash photolysis experiments in conjunction with e.s.r. measurements were carried out. As can be seen from Figure 3, three resonance absorptions were observed. The two resonance bands at the highest and lowest magnetic field appeared at the same magnetic field strength as the weak doublet in the case of continuous irradiations. Accordingly, they are reasonably assigned to the diphenylphosphinoyl radical ( $g$  2.0035 and  $a_p$  36.5 mT).<sup>6</sup> Another absorption band was found at  $g$  2.0008 which can be reasonably assigned to a carbon-centred  $\sigma$  radical.<sup>10-18</sup> Since this signal was formed during the flash simultaneously with the signals of the phosphinoyl radical, it was ascribed to the trimethylbenzoyl radical which is a  $\sigma$  radical, whose small couplings are not resolved on the wide sweep used to contract the spectrum. From the fact that all the signals were formed



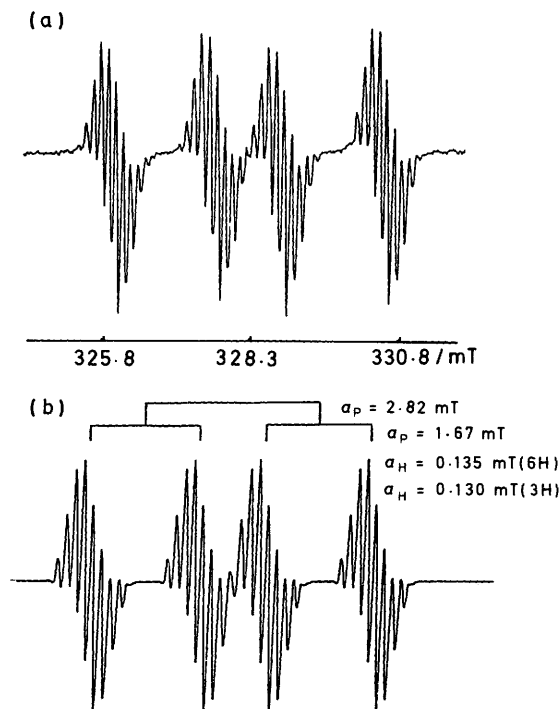
A similar radical (II) was recently detected by Alberti *et al.*,<sup>9</sup> in the reaction of diethylphosphonoyl radicals with diethyl benzoylphosphonate.



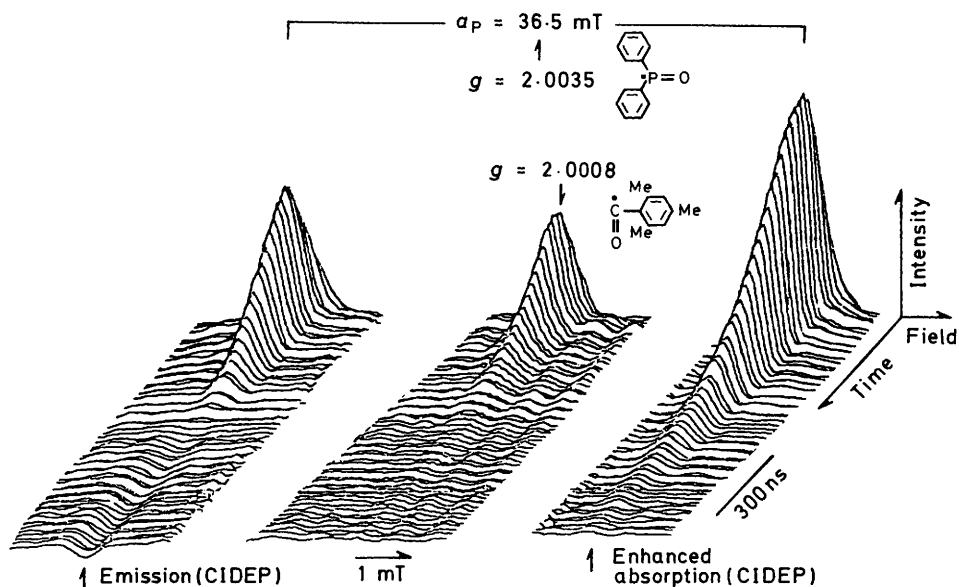
during the 20 ns flash it is inferred that the photodissociation of TMDPO according to reaction (1) occurs very rapidly. This is in agreement with evidence from flash photolysis experiments

in conjunction with optical absorption measurements that the lifetime of the precursor of the radicals, *i.e.*, singlet and/or triplet excited states of TMDPO, is less than 1 ns.<sup>3</sup>

**Decay of diphenylphosphinoyl radicals.** As can be seen from Figure 3, the lines of the phosphinoyl radical decayed in different modes; at the lower magnetic field strength, the absorption decayed after the flash up to a time of about 600 ns and subsequently an emission was formed. At the higher magnetic field strength, the latter process was paralleled by the formation of an enhanced absorption. These effects are

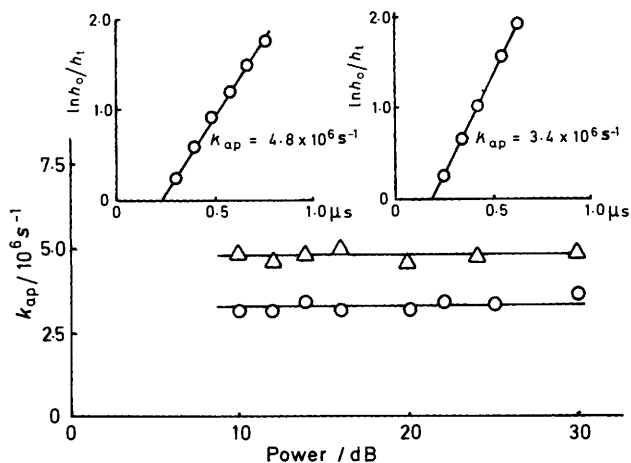


**Figure 2.** (a) E.s.r. spectrum recorded at  $328 \pm 10$  mT during the continuous photolysis of TMDPO in degassed benzene solution (0.1M) at room temperature; (b) computer-simulated e.s.r. spectrum of radical (I)

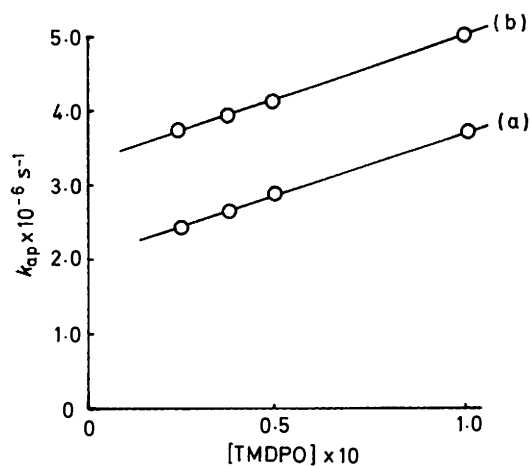


**Figure 3.** Time dependence of the transient e.s.r. spectrum recorded after irradiation of a solution of TMDPO in benzene (0.1M) with a 20 ns flash of 337.1 nm light

indicative of chemically induced dynamic electron spin polarization (CIDEP) due to the radical-pair mechanism.<sup>19</sup> The initial decay of both signals followed first-order kinetics as is demonstrated by the two insets in Figure 4. The apparent first-order rate constants ( $k_{ap}$ ) at the lower and the higher magnetic field strength are  $3.4 \times 10^6 \text{ s}^{-1}$  and  $4.8 \times 10^6 \text{ s}^{-1}$ , respectively. Since the values of  $k_{ap}$  are independent of the microwave power, as is shown in Figure 4, the measured decay rates are deduced to essentially reflect the rate of the addition of phosphinoyl radical to TMDPO according to reaction (3). Since the concentration of TMDPO was much larger than that of the phosphinoyl radicals, the decay is considered to follow pseudo-first-order kinetics. This consideration was confirmed by a linear relationship between the concentration of TMDPO and  $k_{ap}$  as shown in Figure 5. The straight line intersects the ordinate, indicating that apart from the addition reaction to TMDPO phosphinoyl radicals undergo another reaction for example addition to

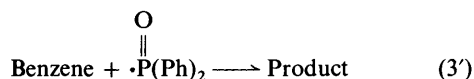


**Figure 4.** Plot of the first-order rate constant  $k_{ap}$  of the decay of e.s.r. absorption of the diphenylphosphinoyl radical vs. the microwave power. The inserts show typical first-order plots of the decay of the e.s.r. absorption at low (left) and high (right) magnetic field, respectively



**Figure 5.** Relation between the apparent first-order rate constant  $k_{ap}$  and the concentration of TMDPO at (a) higher and (b) lower magnetic field

benzene (solvent). The fact that  $k_{ap}$  is larger at lower than at higher magnetic field strength indicates the influence of CIDEP due to the radical-pair mechanism. Consequently,  $k_{ap}$  is expected to depend on the relaxation time  $T_1$  and the rate constants of the addition reaction,  $k_3$  and  $k_3'$  according to equations (5) and (6), at higher and lower magnetic field strength, respectively:



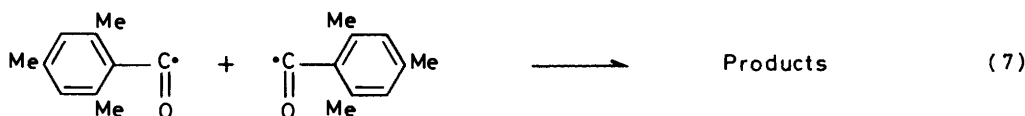
$$k_{ap} = k_3[\text{TMDPO}] + k_3'[\text{Benzene}] - k(T_1) \quad \text{at higher field} \quad (5)$$

$$k_{ap} = k_3[\text{TMDPO}] + k_3'[\text{Benzene}] + k(T_1) \quad \text{at lower field} \quad (6)$$

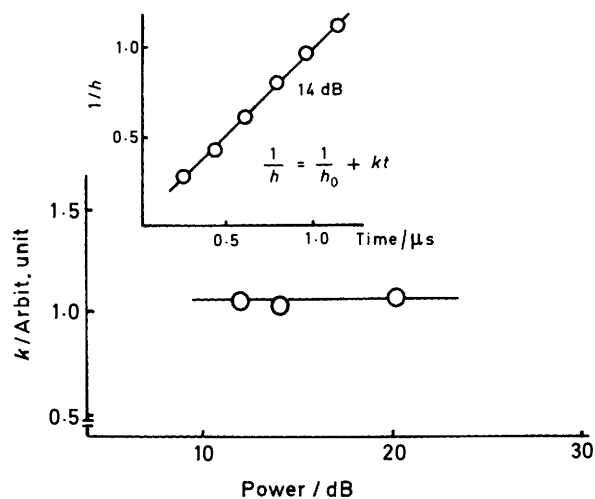
where  $[\text{TMDPO}]$  and  $[\text{benzene}]$  denote the concentration of TMDPO and benzene, respectively, and  $k(T_1)$  is a function of  $T_1$ .

On the basis of the results presented in Figures 4 and 5  $k(T_1) = 7.1 \times 10^5 \text{ s}^{-1}$ ,  $k_3 = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_3' = 2.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . The value of  $1/k(T_1)$  is  $1.4 \times 10^{-6} \text{ s}^{-1}$ , being of the same order of magnitude as  $T_1$  reported for other paramagnetic species.<sup>20</sup> The value of  $k_3$  is seven times larger than those for the reaction of dialkylphosphonoyl radicals with benzene.<sup>21</sup> It is notable, moreover, that the phosphonoyl radical is quite reactive towards the carbonyl group in TMDPO.

*Decay of 2,4,6-trimethylbenzoyl radicals.* The central line at  $g = 2.0008$  decayed according to second-order kinetics as shown in the inset of Figure 6. The rate constant is independent of the microwave power as is also demonstrated in Figure 6. From these results it is inferred that trimethylbenzoyl radicals decay *via* a self-association:<sup>22,23</sup>



An explanation as to why trimethylbenzoyl radicals have little chance to compete with the TMDPO molecules for the diphenylphosphinoyl radical may be found in the following consideration: with initial concentrations of both radicals in the



**Figure 6.** Plot of the second-order rate constant of the decay of the e.s.r. absorption of trimethylbenzoyl radicals *vs.* the microwave power. The insert shows a typical second-order plot of the decay of the e.s.r. absorption

order of  $10^{-6}$ – $10^{-5} \text{ M}$  and at  $[\text{TMDPO}] = 0.1 \text{ M}$ , the rate of the addition reaction (3) is estimated as  $4.1$ – $41 \text{ M s}^{-1}$ . This value is much larger than the rate of coupling of diphenylphosphinoyl radicals with trimethylbenzoyl radicals, namely  $10^{-2}$ – $10^{-1} \text{ M s}^{-1}$ , estimated on the assumption of a coupling rate constant equal to  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ . It appears, therefore, that trimethylbenzoyl radicals could undergo a self-association with a rather high probability.

### Conclusion

In the flash photolysis of TMDPO in conjunction with e.s.r. measurements signals were observed which were ascribed to diphenylphosphinoyl and 2,4,6-trimethylbenzoyl radicals produced by  $\alpha$ -cleavage. It was found that, at a relatively high concentration of TMDPO, the phosphinoyl radical added to the intact TMDPO molecule rather than coupling with trimethylbenzoyl radicals. The latter underwent, under these conditions, a self-association.

In former flash photolysis studies in conjunction with optical absorption measurements<sup>3</sup> triplet excited TMDPO molecules were evidenced, by quenching experiments with naphthalene, to act at least partly as precursors of radicals formed by  $\alpha$ -cleavage. However, for experimental reasons, it could not be decided then, as to what extent bond scission according to reaction (1) involves triplet excited states. In the present work, it was found that the e.s.r. signals ascribed to diphenylphosphinoyl radicals decayed with rates reflecting the reaction of the radicals with intact TMDPO molecules. About 600 ns after the flash the spectra exhibited changes caused by CIDEP according to the radical pair mechanism. Evidence supporting the triplet mechanism for the photodissociation of TMDPO was not

obtained by these e.s.r. studies. In this connection, it is interesting to note that  $\alpha$ -cleavage involving singlet states was observed in the cases of pivaloyldiphenylphosphine oxide and dimethyl and diethyl pivaloylphosphonates.<sup>24</sup>

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