*J. Am. Chem. Soc.* **1996,** *118,* 6477−6489

# Reaction Mechanism of Monoacyl- and Bisacylphosphine Oxide Photoinitiators Studied by $^{31}$P-, $^{13}$C-, and $^{1}$H-CIDNP and ESR

**Urszula Kolczak,**[†,‡] **Günther Rist,**[†] **Kurt Dietliker,***[,§] **and Jakob Wirz**[⊥]

*Physics Department, Ciba-Geigy Ltd., CH-4001 Basel, Switzerland, Additives Research,*
*Ciba-Geigy Ltd., CH-1723 Marly, Switzerland, and Institute of Physical Chemistry,*
*University of Basel, CH-4056 Basel, Switzerland*

*Received October 10, 1995*[⊗]

**Abstract:** $^{31}$P-NMR-CIDNP (CIDNP = chemically induced dynamic nuclear polarization) spectroscopy was applied for the first time to investigate the formation and reaction of phosphorus-centered radicals obtained from phosphorus-containing photoinitiators. $^{13}$C-NMR- and $^{1}$H-NMR-CIDNP and ESR spectroscopies were used as complementary experimental techniques for the elucidation of the photochemistry of these compounds. The large hyperfine coupling constants of the $^{31}$P-nucleus results in a violation of Kaptein's rules, which is the only observation of this kind in $^{13}$C-NMR-CIDNP spectra reported so far. Interpretation of the CIDNP spectra, using a modification of Kaptein's rules for the $^{13}$C-NMR- and $^{1}$H-NMR-CIDNP, consistently shows that all compounds investigated undergo a photoinduced cleavage of the carbonyl−phosphinoyl bond from a triplet state. The fate of the primary radicals is discussed, and it is unambiguously shown by trapping experiments that the novel bisacylphosphine oxide photoinitiators give four radicals in a stepwise process.

## Introduction

The outstanding advantages of radiation curing in terms of economy, ecology, and product quality compared to thermal curing processes are well-known and have led to fast acceptance of this technology in many industrially important coating applications. Furthermore, radiation curing is the basis of most photoimaging processes which are used in the printing and electronics industry.[1−3]

The light-induced radical polymerization of formulations containing suitable reactive double bonds is by far the most widely used method in industry, although other technologies, such as cationic curing processes, are known. The availability of a wide variety of suitable raw materials has allowed the development of formulations which can meet the requirements of many applications. Appropriate photoinitiators, which are one of the key components for the success of this technology, have been available for the curing of clear coatings for many years.[4−6]

In contrast, the curing of pigmented systems by UV or visible light has long been a major challenge.[7−9] The use of pigments in a formulation results in a reduction of the light available for the photoinitiator due to absorption and scattering by the pigment. In general, the photoinitiators used in clear coatings do not have sufficient absorption in that part of the near-UV/vis spectrum, where pigments allow the penetration of light into the formulation. Thus, the use of such photoinitiators in pigmented systems frequently results in an insufficient through-cure and a low cure speed.

Most efforts aimed at the development of new photoinitiators during the past several years have therefore been devoted to the development of new compounds possessing a red-shifted absorption spectrum. As a result, new photoinitiators, such as α-aminoacetophenones[10−12] or thioxanthone derivatives,[13] have recently been introduced as commercial products. Even higher reactivity can be obtained by using combinations of α-amino ketones and thioxanthones which act synergistically.[14] These photoinitiators have allowed the light-induced curing of pigmented systems, such as printing inks or electronic materials, to become another important application of radiation curing.[8] Such initiating systems impart, however, considerable yellowness to the cured formulations and are not suitable for the curing of white pigmented lacquers, where yellowing of the cured film is not at all tolerated.

---

[†] Physical Department, Ciba-Geigy Ltd.

[‡] Present address: Department of Chemistry, University of California, Davis, CA 95616.

[§] Additives Research, Ciba-Geigy Ltd.

[⊥] University of Basel.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints*; Oldring, P. K. T., Ed.; SITA Technology Ltd.: London, 1991; Vols. 1−4.

(2) *Radiation Curing Science and Technology*; Pappas, S. P., Ed.; Plenum Press: New York and London, 1992.

(3) *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier Applied Science: London and New York, 1993; Vols. I−IV.

(4) Dietliker, K. In *Chemistry and Technology of UV and EB Formulation for Coatings, Inks and Paints*; Oldring, P. K. T., Ed.; SITA Technology Ltd.: London, 1991; Vol. 2.

(5) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435.

(6) Davidson, R. S. *J. Photochem. Photobiol., A* **1993**, *73*, 81.

(7) Garratt, P. G. In *Radiation Curing of Polymers II*; Randell, D. R., Ed.; Special Publication No. 89; The Royal Society of Chemistry: Cambridge, 1991; p 103.

(8) Dietliker, K. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier Applied Science: London and New York, 1993; Vol. II.

(9) Catilaz, L.; Fouassier, J. P. *Angew. Makromol. Chem.* **1994**, *218*, 81.

(10) Meier, K.; Rembold, M.; Rutsch, W.; Sitek, F. In *Radiation Curing of Polymers*; Randell, D. R., Ed.; Special Publication No. 64; The Royal Society of Chemistry: London, 1987; p 196.

(11) Desobry, V.; Dietliker, K.; Hüsler, R.; Misev, L.; Rembold, M.; Rist, G.; Rutsch, W. In *Radiation Curing of Polymeric Materials*; Hoyle, C. E., Kinstle, J. F., Eds.; ACS Symposiums Series No. 417; American Chemical Society: Washington, DC, 1990; p 92.

(12) Köhler, M.; Misev, L.; Desobry, V.; Dietliker, K.; Bussian, B. M.; Karfunkel, H. In *Radiation Curing of Polymers II*; Randell, D. R., Ed.; Special Publication No. 89; The Royal Society of Chemistry: Cambridge, 1991; p 163.

(13) Green, A. W.; Timms, A. W.; Green, P. N. *Proc. Conf. Radtech Europe*, Edinburgh, 1991; RadTech Europe: Fribourg, Switzerland, p 636.

(14) Rist, G.; Borer, A.; Dietliker, K.; Desobry, V.; Fouassier, J. P.; Ruhlmann, D. *Macromolecules* **1992**, *25*, 4182.

S0002-7863(95)03421-4 CCC: $12.00

Satisfactory curing of white pigmented lacquers was first achieved using monoacylphosphine oxides as photoinitiators. These compounds have been known for over a decade and can be employed in a variety of applications.[15,16] It is only recently, however, that they have found widespread industrial use, especially in white furniture coatings.[7,8,17]

Acylphosphine oxides are a highly interesting class of photochemically reactive compounds, and investigations of their photochemistry have been published. Upon irradiation, they undergo α-cleavage with high efficiency ($\phi \approx 0.6^{18}$) to produce an aroyl−phosphinoyl radical pair.[18−22] The phosphinoyl radical obtained by photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**; Table 1) has been detected directly in solution using laser flash photolysis techniques[18] and by time-resolved ESR measurements.[20,22,23] A recent publication reports a study of both radical fragments using time-resolved infrared and UV spectroscopies.[24]

The photochemistry of acylphosphine oxides is formally analogous to the photolysis of aryl alkyl ketones. As with the latter compounds, the primary radicals are capable of efficient addition to olefinic compounds. The phosphinoyl radical, however, possesses a number of important structural features which give the aroyl−phosphinoyl radical pair unique properties. Numerous studies have revealed that the phosphinoyl radical is 1−2 orders of magnitude more reactive than the benzoyl radical toward a variety of unsaturated compounds.[18,25−28] This makes these compounds especially useful as photoinitiators for free radical polymerization.

The photochemically-produced radical pair is also of interest due to its uncommon magnetic properties compared to those of the radical pair produced by the photolysis of aryl alkyl ketones. Monoacylphosphine oxide photoinitiators have, for instance, been used in experiments demonstrating spin polarization transfer in radical addition reactions.[23]

Since the absorption of acylphosphine oxides extends well into the visible part of the spectrum, these compounds can absorb sufficient light in the presence of white pigments and act as efficient photoinitiators in such formulations. Moreover, the long-wavelength absorption is due to the aroyl−phosphinoyl chromophore, which is destroyed during the photoreaction. The resulting bleaching allows a progressively deeper penetration of the incident light into the coating layer and makes the curing of thick layers possible. An additional advantage is the disappearance of the yellow hue upon curing, a behavior not exhibited by other photoinitiators which undergo α-cleavage. Therefore, acylphosphine oxides are the most suitable photoinitiators for white lacquer applications.[29,30] White lacquers with increased hiding power require higher concentrations of rutile type $TiO_2$ or higher film thickness. Monoacylphosphine oxide photoinitiators, however, are not well suited for these types of lacquers. This led to the development of a new class of photoinitiators containing two acyl substituents attached to the phosphine oxide unit. Bisacylphosphine oxides have been shown to be superior to monoacylphosphine oxides in these highly demanding applications.[31,32]

Detailed knowledge of the reaction mechanism is a prerequisite for the rational design of more efficient photoinitiators. Therefore, an investigation of the photochemistry of the new bisacylphosphine oxides was undertaken. The phenomenon of chemically induced dynamic nuclear polarization (CIDNP) is observed in nuclear magnetic resonance (NMR) experiments monitoring reactions in which radical species are formed. CIDNP spectroscopy is a powerful tool for the elucidation of radical reactions, since, in contrast to methods using absorption spectroscopy, unequivocal information concerning the structure of the photoproducts and their mode of formation can be obtained. $^1$H- and $^{13}$C-NMR-CIDNP experiments have been successfully used for the determination of the species responsible for the initiation of polymerization by various types of photoinitiators.[11,14,33,34]

The present work represents the first application of $^{31}$P-NMR-CIDNP spectroscopy to investigate the formation and decay of phosphorus-centered radicals formed upon cleavage of photoinitiators.[35,36] Complementary experimental techniques were used to obtain additional information on the photoproducts.

## Experimental Section

**Materials.** The monoacylphosphine oxides **1**−**4** (Table 1) and the bisacylphosphine oxides **5**−**10** (Table 2) were used as starting materials. Monoacylphosphine oxide **1** is commercially available,[37] and bisacylphosphine oxide **8** is part of a commercial photoinitiator blend.[38] Compounds **2**−**9** were synthesized according to the methods given in refs 39 and 40. Compound **10** was synthesized analogously by subsequent addition of 2,4,6-trimethylbenzoyl chloride and 2,6-dimethoxybenzoyl chloride in the acylation step. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TMPO; Aldrich) was used as received. Methyl 2-*tert*-butylacrylate **27** was synthesized according to a procedure

---

[15] Jacobi, M.; Henne, A. *J. Radiat. Curing* **1983**, *19* (4), 16.

[16] Jacobi, M.; Henne, A. *Polym. Paint Colour J.* **1985**, *175*, 636.

[17] Barca, A. *Farbe Lack* **1990**, *96* (2), 422.

[18] Sumiyoshi, T.; Schnabel, W.; Henne, A. *Polymer* **1985**, *26*, 141.

[19] Hayashi, H.; Sakaguchi, Y.; Kamachi, M.; Schnabel, W. *J. Phys. Chem.* **1987**, *91*, 3936.

[20] Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; McLauchlan, K. A.; Stevens, D. G. *J. Chem. Soc., Chem. Commun.* **1987**, 73.

[21] Majima, T.; Konishi, Y.; Boettcher, A.; Kuwata, K.; Kamachi, M.; Schnabel, W. *J. Photochem. Photobiol., A* **1991**, *58*, 239.

[22] Kamachi, M.; Kuwata, K.; Sumiyoshi, T.; Schnabel, W. *J. Chem. Soc., Perkin Trans. 2* **1988**, 961.

[23] Turro, N. J.; Khudayakov, I. V. *Chem. Phys. Lett.* **1992**, *193*, 546.

[24] Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148.

[25] Sumiyoshi, T.; Schnabel, W. *Makromol. Chem.* **1985**, *186*, 1811.

[26] Kajiwara, A.; Konishi, Y.; Morishima, Y.; Schnabel, W.; Kuwata, K.; Kamachi, M. *Macromolecules* **1993**, *26*, 1656.

[27] Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y. *Macromolecules* **1993**, *26*, 7369.

[28] Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; Overeem, T. *Makromol. Chem.* **1988**, *189*, 2769.

[29] Rutsch, W.; Angerer, H.; Desobry, V.; Dietliker, K.; Hüsler, R. *Proc. XVIth Conf. in Organic Coatings - Science and Technology*; State University of New York, Institute for Material Science: New Paltz, NY, 1990; p 423.

[30] Beck, E.; Keil, E.; Lokai, M.; Schröder, J. *Proc. Conf. Radtech Asia 93*, Tokyo, 1993; RadTech Asia: Tokyo, p 181.

[31] Leppard, D.; Dietliker, K.; Hug, G.; Kaeser, R.; Köhler, M.; Kolczak, U.; Misev, L.; Rist, G.; Rutsch, W. *Proc. Radtech'94 North America*, Northbrook, IL, 1994; RadTech International North America: Northbrook, IL, Vol. 2, p 693.

[32] Rutsch, W.; Dietliker, K.; Leppard, D.; Köhler, M.; Misev, L.; Kolczak, U.; Rist, G. *Proc. XXth Internat. Conf. in Organic Coatings Science and Technology*; State University of New York, Institute for Material Science: New Paltz, NY, 1994; p 467. Rutsch, W.; Dietliker, K.; Leppard, D.; Köhler, M.; Misev, L.; Kolczak, U.; Rist, G. *Prog. Org. Coatings* **1996**, *27*, 227.

[33] Borer, A.; Kirchmayr, R.; Rist, G. *Helv. Chim. Acta* **1978**, *61*, 305.

[34] Rutsch, W.; Berner, G.; Kirchmayr, R.; Hüsler, R.; Rist, G.; Bühler, N. In *Organic Coatings - Science and Technology*; Parfitt, G. D., Patsis, A. V., Eds.; Marcel Dekker Inc: New York, 1986; Vol. 8, p 175.

[35] Part of this work has been presented at the XVth IUPAC Symposium on Photochemistry, Prague, July 17−22, 1994; Dietliker, K.; Kolczak, U.; Liegard, A; Rist, G., Wirz, J.; Poster No. 322.

[36] Some investigations using $^{31}$P-CIDNP spectroscopy on other systems have been reported: (a) Levin, Y. A.; Il'yasov, A. V.; Goldfarb, E. I.; Vorokunova, E. I. *Org. Magn. Reson.* **1973**, *5*, 487. (b) Bangert, B. W.; Beatty, R. P.; Kouba, J. K.; Wreford, S. S. *J. Org. Chem.* **1977**, *42*, 3247.

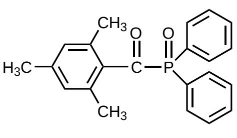
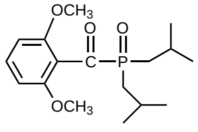
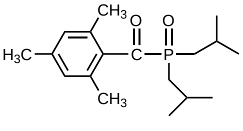
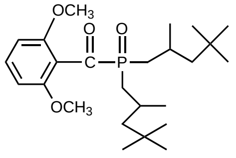
[37] (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1**) is a commercial product of BASF, called Lucirin TPO.

[38] A blend containing 25% bis(2,6-dimethoxybenzoyl)(2,4,4-trimethylpentyl)phosphine oxide (**8**) and 75% 2-hydroxy-2-methylpropiophenone is a commercial product of Ciba-Geigy, called Irgacure 1700.

[39] Ellrich, K.; Herzig, C. Eur. Pat. Appl. 184095 to ESPE Fabrik Pharmazeutischer Präparate GmbH, 1984.

[40] Rutsch, W.; Dietliker, K.; Hall, R. G. US Patent 5218009 to Ciba Geigy AG, 1993.

**Table 1.** Monoacylphosphine Oxide Photoinitiators

| | |
|---|---|
|  **1** | (2,4,6-trimethylbenzoyl)diphenylphosphine oxide |
|  **2** | bis(2-methylpropyl)(2,6-dimethoxybenzoyl)phosphine oxide |
|  **3** | bis(2-methylpropyl)(2,4,6-trimethylbenzoyl)phosphine oxide |
|  **4** | bis(2,4,4-trimethylpentyl)(2,6-dimethoxybenzoyl)phosphine oxide |

reported in the literature.[41] A detailed characterization of the new products is available as supporting information.

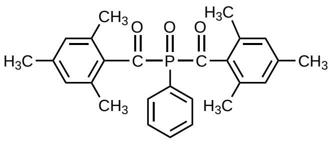
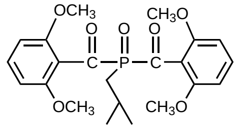
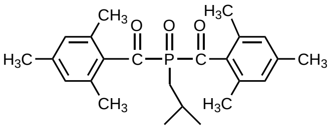
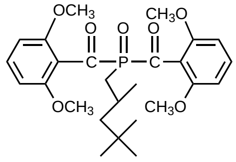
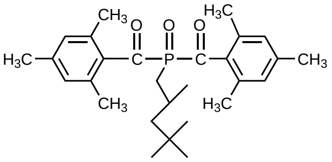
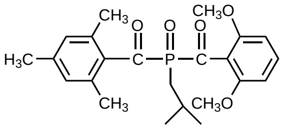
**Experimental Techniques**. The CIDNP measurements were performed on a Bruker AM-200, wide-bore spectrometer with $^{31}$P-, $^{13}$C-, and $^{1}$H-CIDNP probe heads modified for *in situ* irradiation. The light source was a Lambda Physics dye laser operated on diphenylstilbene (404.5 nm) that was pumped by a Questeck excimer laser (XeCl, 308 nm). The wavelength was chosen to model the industrial applications of photoinitiators in the presence of titanium dioxide, where mainly light in the range of 380−450 nm is available for the excitation of the initiator. Perdeuterated acetonitrile was used as a solvent for irradiations. Chemical shifts were measured in parts per million relative to TMS as internal standard ($^{1}$H-NMR and $^{13}$C-NMR spectra) or $H_3PO_4$ as external standard ($^{31}$P-NMR spectra).

In the CIDNP experiments, the pulse sequence $P_{sat}-\tau_1-LP-\tau_2-P_{obs}-AT$ was applied. In this sequence, $P_{sat}$ is a broad band saturation pulse for $^{1}$H-CIDNP experiments and a sequence of 180° radio frequency pulses for the $^{31}$P- and $^{13}$C-CIDNP experiments. LP denotes one or several laser pulses: usually a set of 5−20 pulses with 20 ns duration at a repetition rate of 160 Hz were applied. The number of laser pulses was chosen such that nuclear spin relaxation before the observing pulse was not significant and did not influence the CIDNP intensities. $P_{obs}$ is the observing radio frequency pulse, a 30° rf pulse for the $^{1}$H- and $^{31}$P-CINDP experiments, and a 90° pulse for the $^{13}$C-CIDNP experiments.[42] The parameter AT denotes the acquisition time (0.5−4 s), and $\tau_1$ and $\tau_2$ are variable delay times. Since the NMR absorptions were saturated immediately before the laser pulses, the CIDNP spectra are dominated by the polarized resonances of the photoproducts.

X-band CW ESR experiments were performed on E-9 Varian and Bruker ESP-300E spectrometers with toluene as solvent and a high-pressure mercury lamp as the light source.

**Preparative Irradiations.** Preparative irradiations were performed in degassed acetonitrile using a Philips HPK 125 medium-pressure mercury lamp in a Pyrex immersion vessel. Trapping experiments were performed in the presence of a 5-fold molar excess of the trapping reagent. The products were isolated and purified by the usual preparative and analytical techniques. A detailed characterization of the new products is available as supporting information.

**Table 2.** Bisacylphosphine Oxide Photoinitiators

| | |
|---|---|
|  **5** | bis(2,4,6-trimethylbenzoyl)phenylphospine oxide |
|  **6** | bis(2,6-dimethoxybenzoyl)(2-methylpropyl)phosphine oxide |
|  **7** | bis(2,4,6-trimethylbenzoyl)(2-methylpropyl)phosphine oxide |
|  **8** | bis(2,6-dimethoxybenzoyl)(2,4,4-trimethylpentyl)phosphine oxide |
|  **9** | bis(2,4,6-trimethylbenzoyl)(2,4,4-trimethylpentyl)phosphine oxide |
|  **10** | (2,6-dimethoxybenzoyl)(2,4,6-trimethylbenzoyl)(2-methylpropyl)phosphine oxide |

## Results and Discussion

**Modification of Kaptein's Rules for Use with Acylphosphine Oxides.** The CIDNP spectra of the radical escape and recombination products show emission (E) or enhanced absorption (A). These polarization effects are due to the generation of nuclear spin populations which deviate from the Boltzmann equilibrium distribution. Emission and enhanced absorption disappear with the relaxation time of the nuclear spins, leading to "normal" NMR intensities.

The general features of CIDNP are described as net or multiplet effects. A net effect is observed when the intensity of a singlet, or the sum of the intensities of a multiplet, deviates from that obtained for the equilibrium spin population (either E or A). Simultaneous occurrence of E and A within one multiplet is called a multiplet effect. The pattern of emission, followed by enhanced absorption, from lower to higher magnetic field, is known as an E/A multiplet effect, while the opposite pattern is an A/E multiplet effect.

These effects are explained by the quantitative radical pair theory.[43] Kaptein has condensed this theory into two rules which allow a qualitative analysis of CIDNP spectra.

The rules refer to signs only; i.e., they relate the signs of the electron spin multiplicity $\mu$ of the precursor, of the mode of product formation $\epsilon$ (cage or escape products), and of the magnetic parameters $\Delta g$, $A_i$, $A_j$, $J_{ij}$, and $\sigma_{ij}$ to that of the net

---

(41) Xu, L.-H.; Kündig, E. P. *Helv. Chim. Acta* **1994**, *77*, 1480.

(42) Schäublin, S.; Höhner, A.; Ernst, R. R. *J. Magn. Reson.* **1974**, *13*, 196.

**Table 3.** Kaptein's Rules with the Modifications for the Analysis of $^{13}$C- and $^{1}$H-NMR-CIDNP Spectra of Mono- and Bisacylphosphine Oxides

| | | polarization type | | |
|---|---|---|---|---|
| Kapten's rule | sign of $\Gamma$ | $^{31}$P-CIDNP | $^{13}$C-CIDNP | $^{1}$H-CIDNP |
| net effect | $\Gamma_{ne}$, + | absorption (A) | emission (E) | emission (E) |
| $\Gamma_{ne} = \mu\epsilon\Delta g A_i$ | $\Gamma_{ne}$, − | emission (E) | absorption (A) | absorption (A) |
| multiplet effect | $\Gamma_{me}$, + | emission/absorption pattern (E/A) | | |
| $\Gamma_{me} = \mu\epsilon A_i A_j J_{ij} \delta_{ij}$ | $\Gamma_{me}$, − | absorption/emission pattern (A/E) | | |

effect $\Gamma_{ne}$ (eq 1) or to the "phase" of a multiplet effect $\Gamma_{me}$ (eq 2) of the polarized nuclei *i* and *j*. In eqs 1 and 2, the signs are assigned according to the conventions given by Kaptein.[44]

$$\text{net polarization:}\quad \Gamma_{ne} = \mu\epsilon\Delta g A_i \qquad (1)$$

$$\text{multiplet effect:}\quad \Gamma_{me} = \mu\epsilon A_i A_j J_{ij}\sigma_{ij} \qquad (2)$$

Conversely, these rules may be used to determine the sign of one of the polarization parameters, when those of the other parameters are known. Kaptein's rules hold for most radical reactions. Exceptions may result, if nuclei with large hyperfine coupling constants are involved, which can influence the polarization of other nuclei. This effect may reverse the polarization predicted for nuclei with smaller hyperfine coupling constants.[45−48] Such deviations from the simple rules were observed earlier in $^{1}$H-CIDNP-NMR spectra, where strongly hyperfine coupled $^{13}$C-nuclei influence the CIDNP effects of $^{1}$H-nuclei that are coupled to the same unpaired electron. A modification of Kaptein's rules for this situation has been proposed.[48]

We report here evidence for a violation of Kaptein's rules in $^{13}$C-NMR-CIDNP spectra, which, to our knowledge, is the first observation of this kind reported as yet. The $^{31}$P-nucleus exhibits a much larger hyperfine coupling constant than the relevant $^{13}$C-nucleus. More important, this hyperfine coupling is larger than the difference of the *g* values in frequency units. Therefore, the quantitative radical pair theory had to be used to define the limits of the qualitative rules for the spin systems investigated.[49] The results of these calculations are summarized by the modifications of Kaptein's rules shown in Table 3.

Using the modified signs of Table 3 for the interpretation of net and multiplet effects in the spectra of monoacyl- and bisacylphosphine oxides, a consistent interpretation of the CIDNP effects in the $^{31}$P-, $^{13}$C- and $^{1}$H-NMR spectra is obtained. These modified rules are thus used throughout the following discussion.

**Investigated Compounds.** The structures of the monoacyl- and bisacylphosphine oxide compounds investigated are collected in Tables 1 and 2. All compounds are highly reactive photoinitiators for the polymerization of olefinic compounds.

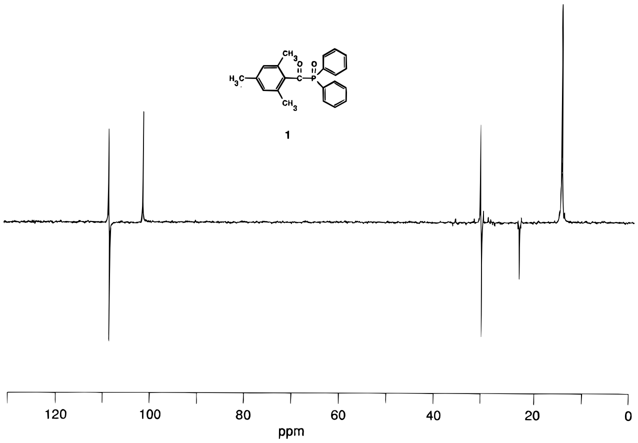


**Figure 1.** $^{31}$P-NMR-CIDNP spectrum of monoacylphosphine oxide **1**.

(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1**) has been studied before by using other experimental techniques.[18−24,50] This compound affords easily interpretable spectra and was therefore included in this study as a reference. The bisacylphosphine oxide **5** was selected for its substitution pattern which is analogous to that of **1**. Similarly, the new monoacylphosphine oxides **2**−**4** were investigated as monofunctional models for the corresponding bisacylphosphine oxides **6**−**9**, possessing analogous substituents at phosphorus and on the benzoyl moiety, respectively.

While the bisacylphosphine oxides **5**−**9** are substituted by two identical aroyl substituents at phosphorus, compound **10** has two different types of benzoyl substituents. This photoinitiator was used to obtain information on the relative reactivity of the 2,4,6-trimethylbenzoyl and the 2,6-dimethoxybenzoyl groups within the same molecule.

All compounds carry two *ortho* substituents on the benzoyl moiety. Such a substitution pattern is typical for this class of photoinitiators. Bulky groups in the *ortho* position shield the carbonyl group from nucleophilic attack and thereby provide the solvolytic stability which is required for industrial applications.[32]

Both phenyl and alkyl substitutents at phosphorus were investigated, since both substitution patterns are found in commercial photoinitiators. Branched alkyl groups were selected since they render the compounds more soluble in technical formulations.[32]

**$^{31}$P-NMR-CIDNP Studies of Monoacylphosphine Oxides.** A typical $^{31}$P-CIDNP spectrum, obtained upon irradiation of compound **1** in acetonitrile, is shown in Figure 1. Pentavalent phosphorus, substituted by double-bonded oxygen, resonates between 0 and 50 ppm, while the resonances of trivalent phosphorus are observed at lower field strength (approximately 100−130 ppm). Products are observed in both regions for all the initiators investigated here.

---

(43) (a) Kaptein, R. In *Chemically Induced Magnetic Polarization*; Muus, L. T., Atkins, P. W., McLauchlan, K. A., Pedersen, K. B., Eds.; Nato Advanced Study Institutes Series; M. Reidel Publishing Co.: Dordrecht, The Netherlands, 1977. (b) Lepley, A. R.; Closs, G. L. *Chemically Induced Magnetic Polarization*; J. Wiley and Sons: New York, 1973. (c) Pedersen, J. B. *Theories of Chemically Induced Magnetic Polarization;* Odense University Press: Odense, Denmark, 1979. (d) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z. Buchachenko, A. L. In *Spin Polarization and Magnetic Effects in Radical Reactions*; Molin, Yu. N., Ed.; Elsevier: Amsterdam, 1984.

(44) Kaptein, R. *Chem. Commun.* **1971**, 732.

(45) Salikhov, K. M. *Chem. Phys.* **1982**, *64*, 371.

(46) Hutton, R. S.; Roth, H. D.; Bertz, S. H. *J. Am. Chem. Soc.* **1983**, *105*, 6371.

(47) Hore, P. J.; Stob, S.; Kemmink, J.; Kaptein, R. *J. Phys. Lett.* **1983**, *98*, 409.

(48) Roth, H. D.; Hutton, R. S.; Hwang, K. C.; Turro, N. J.; Welsh, K. M. *J. Phys. Chem.* **1989**, *93*, 5697.

(49) Kolczak, U. Ph.D. Thesis, University of Basel, Switzerland, 1995.

(50) Independently of this work, an investigation of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (**1**) using $^{31}$P-NMR spectroscopy has been performed: Turro, N.; Koptyug, I. V.; Sluggett, G. W.; Bentrude, W. G. To be published.

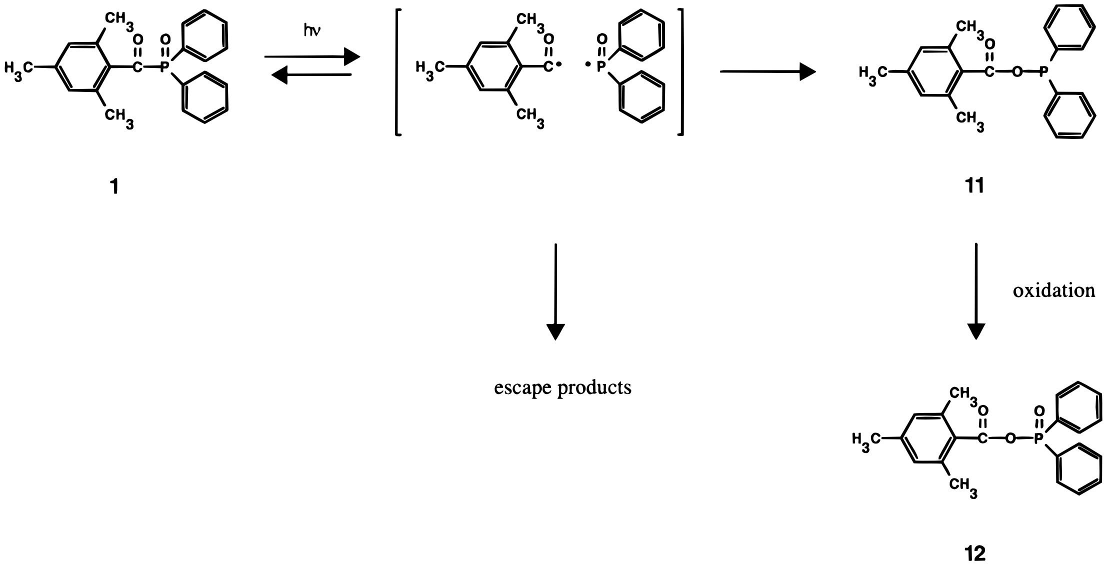


**Figure 2.** Cage recombination products of monoacylphosphine oxide **1**.

***Cage Recombination Products.*** The primary photochemical reaction step of compound **1** has been shown to be the cleavage of a carbon−phosphorus bond (α-cleavage),[15,18,22,25] leading to a spin-correlated benzoyl and phosphinoyl radical pair.

The radicals obtained by the photoinduced cleavage can reencounter after diffusion and undergo either recombination or disproportionation reactions. As disproportionation is not an important reaction for the compounds investigated in this study (see $^1$H-NMR-CIDNP experiments), recombination processes predominate for the primary radicals of **1** in the absence of a trapping agent. The most efficient recombination process is regeneration of the starting material **1**. This process is manifested by the strong enhanced absorption at 14.88 ppm.

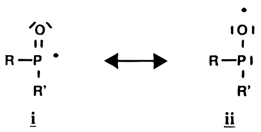
This resonance can be analyzed using Kaptein's rule (eq 1). The values for the two $g$ factors are known,[22,51] and the calculated sign of $\Delta g$ is positive:

$$\Delta g = g_{\text{phosphinoyl}} - g_{\text{carbonyl}} = 2.0036 - 2.0009 = 0.0027$$

ESR experiments with the initiators investigated here indicate that the substitution of the benzoyl and phosphinoyl radicals does not lead to a significant deviation from this number. The hyperfine coupling constant, $A_P$, is known to be positive.[36a] Since the observed resonance shows enhanced absorption and is due to a cage recombination product, positive signs for $\Gamma_{ne}$ (Table 3) and $\epsilon$ have to be used in eq 1. Hence, the sign for $\mu$ is positive, and *the recombination product must be formed from a triplet precursor of a radical pair*. This result is in agreement with the conclusions from chemically induced dynamic electron polarization (CIDEP) studies of compound **1** and of the related (2,6-dimethoxybenzoyl)diphenylphosphine oxide.[20,22]

A second resonance at 101.9 ppm exhibiting positive polarization (enhanced absorption) must arise from a trivalent phosphorus atom in a product produced by a cage recombination process. It is assigned to [(2,4,6-trimethylbenzoyl)oxy]diphenylphosphine **11** (Figure 2).

The formation of product **11** can be explained by the reaction of the benzoyl radical with the oxygen atom of the phosphinoyl counterpart. While the spin density of the $\sigma$-type benzoyl radical is largely localized on the carbon atom, significant spin densities are found on both the phosphorus and oxygen atoms in phosphinoyl radicals.[52] An adequate description for this situation is given by the superposition of two canonical structures, **i** and **ii**, with the unpaired electron located on either phosphorus or oxygen.



The phosphinoyl oxygen thus possesses sufficient spin density to undergo radical reactions such as the recombination to give **11**. The chemical shift of the proposed structure **11** is in good agreement with the value of 103.2 ppm (in $CD_2Cl_2$ as solvent) reported for the same compound in the literature.[53] Furthermore, the same reaction product was independently proposed on the basis of other experimental evidence.[24]

In solution, [(2,4,6-trimethylbenzoyl)oxy]diphenylphosphine (**11**) is slowly oxidized to the corresponding phosphine oxide **12**. In the $^{31}$P-CIDNP spectrum, the weak absorption line at 29.07 ppm is assigned to compound **12**, as it was confirmed by comparison with the spectrum of independently synthesized **12**. Apparently, this product is formed in a time interval which is short compared to the nuclear relaxation time of the phosphorus spin.

Analogous cage recombination products were detected upon irradiation of the monoacylphosphine oxides **2**−**4**. The chemical shifts of the corresponding resonances are collected in Table 4. Compared with the CIDNP spectrum of **1**, the phosphorus resonances of these compounds are shifted to lower field by approximately 22−26 ppm for pentavalent phosphorus and 24−29 ppm for trivalent phosphorus. These shifts are due to the replacement of the phenyl group on phosphorus in **1** by alkyl groups in **2**−**4**. As for **1**, all these resonances exhibit positive polarization which is consistent with cage recombination of radicals formed from a triplet precursor. Hence, all of the monoacylphosphine oxides investigated undergo the same cage reaction as compound **1**.

***Escape Products.*** When primary radicals leave the solvent cage and encounter other radicals, escape products are formed. Clearly, escape products formed from phosphorus radicals can

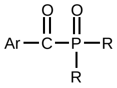
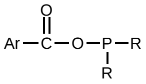
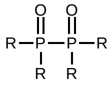
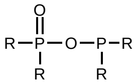
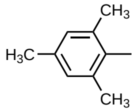
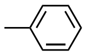
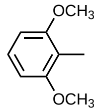
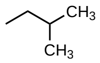
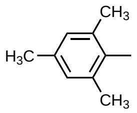
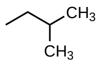
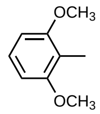
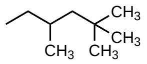
---

[51] Benn, R.; Dreeskamp, H. *Z. Phys. Chem.* **1976**, *101*, 11.

[52] Kochi, J. K. *Free Radicals*; Wiley & Sons: New York, 1973; Vol. II, p 616.

[53] Brierley, J.; Dickstein, J. I.; Trippett, S. *Phosphorus Sulfur* **1979**, *7*, 167.

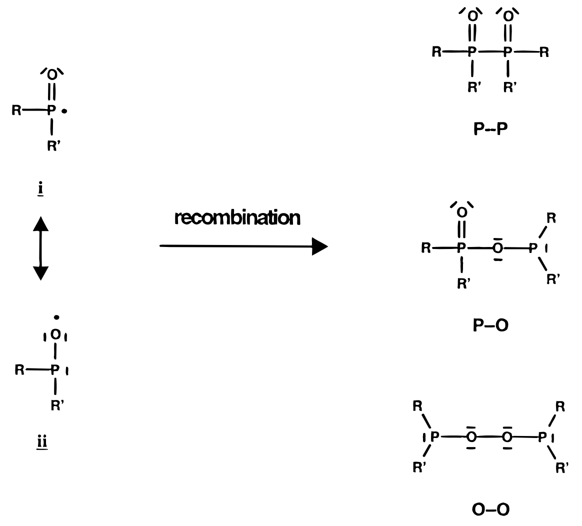
**Table 4.** $^{31}$P-NMR Data of Monoacylphosphine Oxides **1**−**4** and Their Photoproducts[a]

| | | monoacylphosphine oxides **1**−**4** | photoproducts | | | | |
|---|---|---|---|---|---|---|---|
| | |  $\mathrm{Ar{-}C(=O){-}P(=O)(R){-}R}$ <br> δ |  $\mathrm{Ar{-}C(=O){-}O{-}P(R){-}R}$ <br> δ |  $\mathrm{R{-}P(=O)(R){-}P(=O)(R){-}R}$ <br> δ |  $\mathrm{R{-}P(=O)(R){-}O{-}P(R){-}R}$ | | |
| Ar | R | | | | $\delta_{P(V)}$ | $\delta_{P(III)}$ | $^{2}J_{P-P}$ |
|  |  | 14.18 (A) | 101.92 (A) | 23.04 (E) | 31.02 (A/E) | 109.02 (A/E) | +24.60 |
|  |  | 39.80 (A) | 130.30 (A) | 44.89 (E) | 53.20 (A/E) | 132.60 (A/E) | +8.90 |
|  |  | 41.79 (A) | 131.09 (A) | 44.89 (E) | 53.20 (A/E) | 132.60 (A/E) | +8.90 |
|  |  | 39.51 (A)<br>40.24 (A) | 131.13 (A)<br>131.45 (A) | 42−48 (E) | 42−54<br>(A/E) and E/A) | 132−136 | 7.18[b]<br>8.07[b] |

[a] Chemical shift values δ of $^{31}$P nuclei in parts per million relative to external $H_3PO_4$. Coupling constants in hertz. A = enhanced absorption. E = emission. [b] Overlapping resonance lines of different enantiomers. Only data of clearly distinguished resonances are given.

be detected by $^{31}$P-CIDNP spectroscopy (for the discussion of compounds such as the benzil derivative **15**, containing no phosphorus atom, see the section on $^{13}$C-NMR- and $^{1}$H-NMR-CIDNP experiments).

The spin density distribution in the phosphinoyl radical suggests that three possible types of escape products may be obtained by recombination of these radicals, compounds having a P−P, a P−O or a O−O bond:



The formation of the dimer with a P−P bond, tetraphenylbis(phosphine oxide) (**13**), and that with a P−O bond, diphenylphosphinous diphenylphosphinic acid anhydride (**14**), was indeed observed in the $^{31}$P-CIDNP spectrum obtained from **1** (Figure 3, Table 4). No evidence for the formation of the O−O recombination product was found. This is not surprising in view of the expected instability of this structure.

The chemical shifts and the polarization of the resonances attributed to products **13** and **14** are given in Table 4. In agreement with Kaptein's rules, the signals of the escape products carry opposite net polarization with respect to the cage recombination products.

Since the two phosphorus nuclei in tetraphenylbis(phosphine oxides) of type **13** are magnetically equivalent, no $^{31}$P−$^{31}$P spin coupling can be observed,[54] and only one emission line at 23.04 ppm was recorded. This contrasts with product **14** which contains two magnetically nonequivalent phosphorus nuclei bridged by an oxygen atom. This compound gives rise to two doublets, at 109.02 ppm (trivalent phosphorus) and at 31.02 ppm (pentavalent phosphorus), with a coupling constant of 24.6 Hz, which show a dominant A/E multiplet polarization pattern.

In order to determine the small net effect, the separation method was applied. Separation of the net (escape) and the multiplet (free radical encounter) effects is possible by addition of spectra taken after 45° and 135° radio frequency pulses. This treatment yields the contribution of the pure net polarization, while subtraction of the two spectra affords the signals resulting from the multiplet effect.[55] Application of this method confirmed a weak emission net effect which is in agreement with Kaptein's rule. This is evidence for the formation of **14** via two channels: either as an escape product after leaving the primary cage, or by recombination of free phosphinoyl radical with $\Delta g = 0$.

Signs of coupling constants cannot usually be deduced from conventional NMR spectra. CIDNP spectroscopy offers a simple means to determine this parameter from experimental data, provided that the resonance shows a multiplet effect. The second sign rule (eq 2) contains the sign of the nuclear spin−spin coupling constant $J_{ij}$. Hence, if the other parameters in eq 2 are known, the sign of $J_{ij}$ can be determined. Since the hyperfine coupling constant of the two phosphorus nuclei is known to be positive,[36a] and the products are formed by free radical encounter ($\mu$ and $\epsilon$ positive), the sign of the $^{2}J_{P-P}$ coupling constant must be positive. It has been established that the magnitude and sign of one-, two-, or three-bond phosphorus−

---

(54) Frey, G.; Lesiecki, H.; Lindner, E.; Vordermaier, C. *Chem. Ber.* **1979**, *112*, 763.

(55) Vollenweider, J. K.; Fischer, H. *Chem. Phys.* **1986**, *108*, 365.

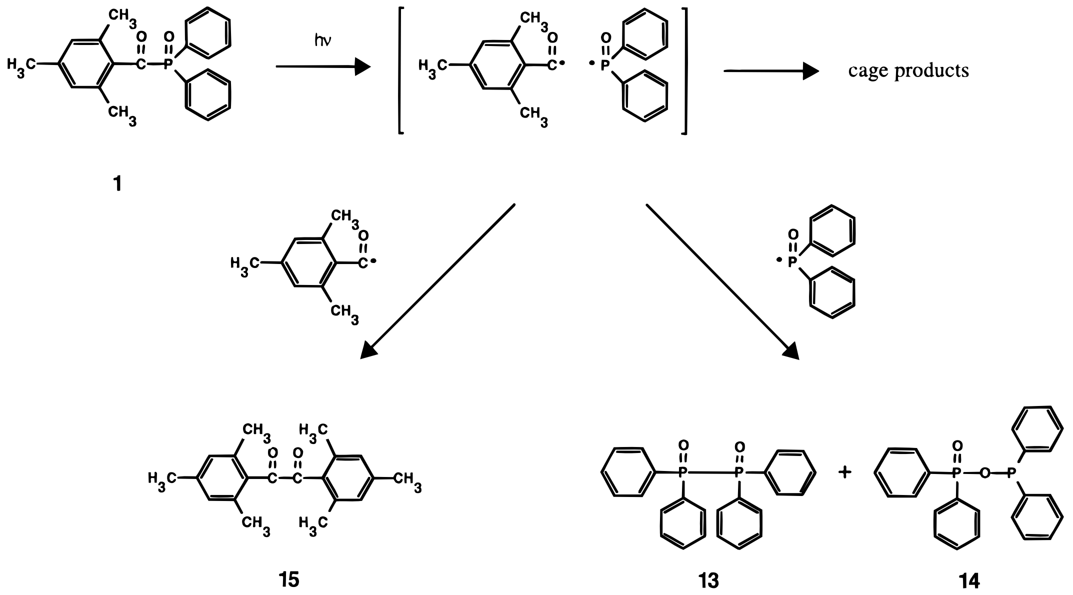
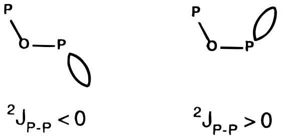


**Figure 3.** Escape products of monoacylphosphine oxide **1**.

phosphorus coupling constants depends on the orientation of the lone pairs with respect to the phosphorus(V)−oxygen bond along the coupling path.[56] For compound **14**, the positive sign of the $^2J_{P-P}$ coupling constant points to a *cisoid* arrangement:



The resonances of the escape products obtained upon irradiation of the monoacylphosphine oxides **2**−**4** were analyzed in the same way. Chemical shifts and coupling constants, including the signs, are shown in Table 4. As was found for the signals of the cage products, the phosphorus resonances of these compounds are shifted to lower field by 11−27 ppm, compared to the photoproducts of **1**. Again, this effect is attributed to the replacement of aromatic by alkyl substituents on phosphorus.[57] The signals of the bis(phosphine oxides) and the phosphinous phosphinic acid anhydride derivatives derived from the monoacylphosphine oxides **2** and **3** show the same A/E multiplet effect as compounds **13** and **14**; therefore, the sign of the $^2J_{P-P}$ coupling constants must be positive (Table 4). Note that the magnitude of the $^2J_{P-P}$ coupling constant depends on the chemical substitution pattern. The multiplet effects of the escape product stemming from **4** were not analyzed due to overlapping resonances of up to eight diastereomers.

**$^{31}$P-NMR-CIDNP Studies of Bisacylphosphine Oxides.** Bisacylphosphine oxides **5**−**10** were irradiated under the same conditions as the monoacylphosphine oxides. The $^{31}$P-CIDNP spectrum of **5** is shown as an example in Figure 4.

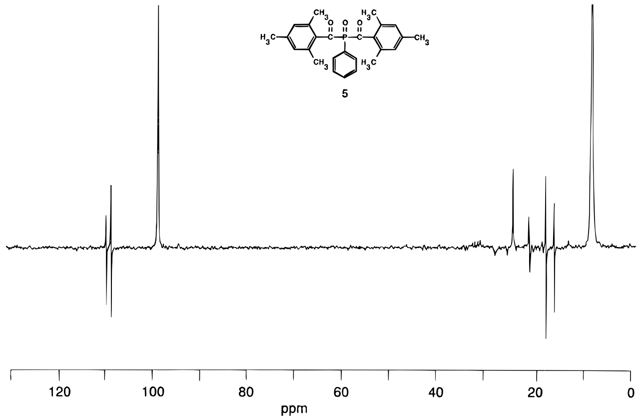


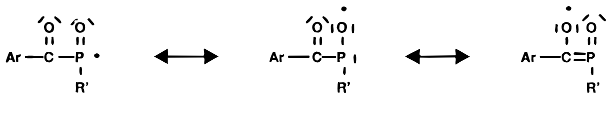
**Figure 4.** $^{31}$P-NMR-CIDNP spectrum of bisacylphosphine oxide **5**.

A comparison of the spectra obtained upon irradiation of monoacylphosphine oxide **1** (Figure 1) and bisacylphosphine oxide **5** reveals that both compounds afford the same type of resonances in the regions typical for trivalent and pentavalent phosphorus. The spectrum obtained from compound **5** is typical for all spectra obtained from bisacylphosphine oxides. The spectrum is more complex than that arising from **1**, since some of the photoproducts are produced as diasteromeric mixtures and secondary photochemical reactions occur (see below).

The chemical shifts and polarizations of all bisacylphosphine oxides investigated and their photoproducts are shown in Table 5.

***Cage Recombination Products.*** The phosphorus resonance at 7.92 ppm of the phosphorus atom in the starting material **5** is the most prominent signal in this spectrum. The resonance carries a positive polarization (enhanced absorption) and is evidence for in-cage recombination of the spin-correlated benzoyl−phosphinoyl radical pair. According to Kaptein's rule, the latter must have been formed from a triplet state precursor. Hence, as with monoacylphosphine oxides, the primary photoreaction of **5** and all other bisacylphosphine oxides investigated in this study is α-cleavage from a triplet excited state (Figure 5). The subsequent cleavage of the second benzoyl group in the bisacylphosphine oxide structure is discussed below.

Irradiation of a bisacylphosphine oxide yields an acylphosphinoyl radical. In addition to the canonical structures **i** and **ii**, which are analogous to those shown above, a third structure, **iii**, contributes to the description of this phosphinoyl radical.

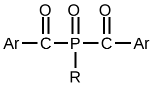
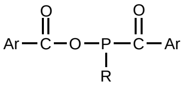
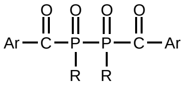
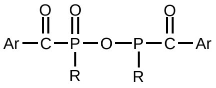
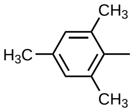
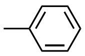
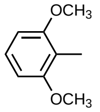
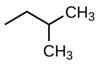
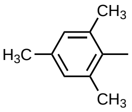
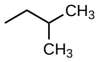
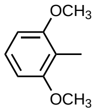
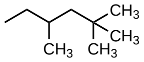
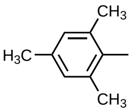
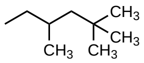


---

[56] Gil, V. M. S.; von Philipsborn, W. *Magn. Reson. Chem.* **1989**, *27*, 409.

[57] Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Spectroscopy*; Pergamon Press: Oxford, 1966; p 1066.

**Table 5.** $^{31}$P-NMR Data of Bisacylphosphine Oxides **5**−**9** and Their Photoproducts[a]

| | | bisacylphosphine oxides **5**−**9** | photoproducts | | | | |
|---|---|---|---|---|---|---|---|
| | |  $\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R}{\mid}}{\overset{\overset{O}{\|}}{P}}{-}\overset{\overset{O}{\|}}{C}{-}Ar}$ |  $\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}O{-}\underset{\underset{R}{\mid}}{P}{-}\overset{\overset{O}{\|}}{C}{-}Ar}$ |  $\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R}{\mid}}{\overset{\overset{O}{\|}}{P}}{-}\underset{\underset{R}{\mid}}{\overset{\overset{O}{\|}}{P}}{-}\overset{\overset{O}{\|}}{C}{-}Ar}$ |  $\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R}{\mid}}{\overset{\overset{O}{\|}}{P}}{-}O{-}\underset{\underset{R}{\mid}}{P}{-}\overset{\overset{O}{\|}}{C}{-}Ar}$ | | |
| Ar | R | δ | δ | δ | $\delta_{P(V)}$ | $\delta_{P(III)}$ | $^2J_{P-P}$ |
|  |  | 7.92 (A) | 98.78 (A) | 23.84 (E) | 15.78 (A/E) | 109.50 (A/E) | +5.9 |
| | | | | 25.61 (E) | 17.54 (A/E) | 104.48 (A/E) | +11.2 |
|  |  | 25.11 (A) | 111.75 (A) | 36.28 (E) | 28.92 (E/A) | 123.80 (E/A) | −6.8 |
| | | | | 38.34 (E) | 30.34 (A/E) | 121.33 (A/E) | +6.8 |
|  |  | 29.34 (A) | 117.04 (A) | 43.50 (E) | 32.20 (E/A) | 133.42 (E/A) | −13.6 |
| | | | | 44.43 (E) | 32.91 (E/A) | 128.64 (A/E) | +7.4 |
|  |  | | | | | | 7.4[b] |
| | | 25.35 (A) | 112.39 (A) | 32−40 (E) | 27.5−31.0 | 119−128 | 6.28b |
| | | | 112.61 (A) | | | | 10.32[b] |
|  |  | 29.43 (A) | 117.29 (A) | 36−46 (E) | 30−35 | 126−137 | *c* |
| | | | 117.95 (A) | | | | |

[a] Chemical shift values δ of $^{31}$P-nuclei in parts per million relative to external $H_3PO_4$. Coupling constants in hertz. A = enhanced absorption. E = emission. [b] Overlapping resonance lines of different enantiomers. Only data of clearly distinguished resonances are given. [c] Not determined due to the low signal to noise ratio.

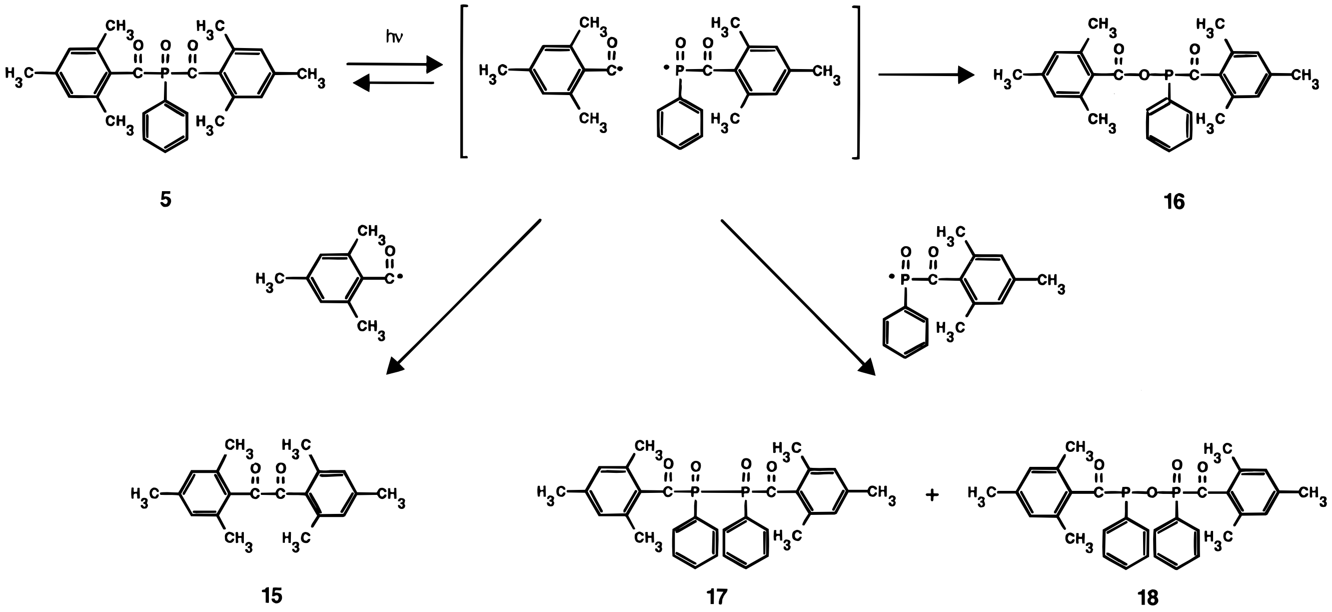
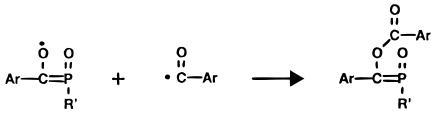


**Figure 5.** Cage recombination and escape products of bisacylphosphine oxide **5**.

Combination of the benzoyl radical with the phosphinoyl oxygen (formula **ii**) formed from bisacylphosphine oxide **5** results in the formation of product **16** (Figure 5). This compound is identified in the $^{31}$P-CIDNP spectrum by the resonance at 98.78 ppm (enhanced absorption). This reaction pathway is analogous to that found for monoacylphosphine oxides, and is valid for all bisacylphosphine oxides investigated here.

In contrast to the phosphinoyl radicals obtained from the monoacylphosphine oxides, the P=O moiety of radicals formed from bisacylphosphine oxides is substituted by two different groups. If the reaction of these radicals results in the introduction of a third unique substituent on phosphorus, an asymmetric center is formed at this atom. As a consequence, diastereomeric mixtures are formed, when the product contains other asymmetric centers in the aliphatic side chain or at a second phosphorus atom. This is the case for the products obtained from **8** and **9** which give rise to two resonance lines, attributable to the diastereomeric products.

Resonances carrying enhanced absorption were observed at 20 ppm for **5** and at about 39 ppm for **6** and **8**. This polarization reveals that the products must arise from cage recombination. Although no proof for the structures is available as yet (the resonances are therefore not included in Table 5), these signals are best attributed to products of structure **iv**, which are expected from the recombination described below.



iii iv

These products are expected to be less stable than the other photoproducts and, as yet, have eluded further characterization.

***Escape Products.*** The photolysis of bisarylphosphine oxides yields escape products that are similar to those observed with monoacylphosphine oxides. Compounds **17** and **18** are the phosphorus-containing products obtained from **5** (Figure 5). The two asymmetric phosphorus atoms in these structures give rise to two pairs of resonance signals (Figure 4). In agreement with Kaptein's rules, the signals of compound **17** show emission-type polarization, while A/E multiplet polarization is found for the trivalent and pentavalent phosphorus atoms in structure **18**. The $^{2}J_{\mathrm{P-P}}$ coupling constants were determined to be positive, which is attributed to a *cisoid* arrangement of the phosphorus(V)−oxygen bond and the electron lone pair on phosphorus(III).

Analogous signals are observed in the spectra obtained from bisacylphosphine oxides **6**−**9**. Due to the presence of an additional asymmetric carbon atom in each alkyl group, eight enantiomeric pairs are expected for the escape products of **8** and **9** which contain two phosphorus atoms. The low signal-to-noise ratio of the CIDNP resonances did not allow a detailed analysis of these resonances, and only a range for the chemical shifts is given in Table 5.

Interestingly, the signals of one pair of enantiomers obtained from compound **6** exhibit an E/A multiplet polarization and a negative $^{2}J_{\mathrm{P-P}}$ coupling constant (Table 5), while the other pair carries opposite polarization and exhibits a positive coupling constant. These results indicate that the product pairs have distinctly different conformations. The same situation is encountered with the corresponding enantiomeric pairs obtained from **7** (Table 5).

**$^{31}$P-NMR-CIDNP Spectrum of (2,6-Dimethoxybenzoyl)-(2′,4′,6′-trimethylbenzoyl)(2-methylpropyl)phosphine Oxide (10).** Photoinitiator **10** is a particularly interesting compound, since the phosphorus atom is substituted by both a 2,6-dimethoxybenzoyl and a 2,4,6-trimethylbenzoyl group. The data of the (acyloxy)phosphine derivatives, obtained from the $^{31}$P-NMR-CIDNP spectrum of this photoinitiator, are shown in Table 6.

This molecule can undergo cleavage between phosphorus and either of the two benzoyl groups from its excited state, resulting in the formation of two different pairs of primary radicals (Figure 6). Recombination within the solvent cage gives the starting material **10** and the two P−O recombination products **19** and **20**.

Cross combination of the primary radicals can lead to the formation of the symmetrically substituted bisacylphosphine oxides **6** and **7** and the acyloxy-substituted acylphosphines **21** and **22**. The resonances of product **6** at 25.11 and of product **7** at 29.34 ppm, respectively, are observed in the CIDNP spectrum. The fact that both signals exhibit similar polarizations is consistent with free radical encounter and subsequent combination of two radicals with very different *g* values.

**Table 6.** $^{31}$P-NMR Chemical Shift Values of Bisacylphosphine Oxide **10** and Its (Acyloxy)acylphosphine Photoproducts[a]

| bisacylphosphine oxide **10** | (acyloxy)acylphosphine photoproducts |
|---|---|
| 27.55 (A) | **19**[b] 110.72 (A, vs)<br>**20**[b] 115.92 (A, vw)<br>**21** 111.75 (A, w)<br>**22** 117.04 (A, w) |

[a] Chemical shift values $\delta$ of $^{31}$P-nuclei in parts per million relative to external $H_3PO_4$. Intensity of resonance lines: vs = very strong, w = weak, vw = very weak. A = enhanced absorption. [b] Tentative structure assignment.

The resonances attributed to **21** (111.75 ppm) and **22** (117.04 ppm) are unequivocally identified by comparison with the resonances of the same products observed in the $^{31}$P-NMR-CIDNP spectra of compounds **6** and **7**. The two other absorptions are tentatively attributed to **19** and **20** on the basis of their chemical shifts. In agreement with Kaptein's rule, the resonances of these compounds show enhanced absorption. From the CIDNP intensities of the resonances of products **6, 7, 21**, and **22**, the ratio of the rate constant $k_{\mathrm{P(V)}}$ for the formation of bisacyclphosphine oxides to the rate constant $k_{\mathrm{P(III)}}$ for the formation of (benzoyloxy)phosphines is approximately 10, assuming similar relaxation times for P(III) and P(V).

From inspection of the $^{31}$P-NMR-CIDNP spectrum, it is apparent that the signal for product **19** is much more intense than that of **20**. This could be due to the more efficient photochemical cleavage of the 2,4,6-trimethylbenzoyl group in **10**. However, differences in the steric bulk of the 2,4,6-trimethylbenzoyl and 2,6-dimethoxybenzoyl radicals, resulting in a more efficient recombination of the former with the oxygen atom of the phosphorus-containing radical, could also explain these experimental results. The available data do not allow these two pathways to be distinguished. The ratio of the intensity of the resonance line of **19** to that of **20** in the $^{31}$P-CIDNP spectrum is approximately 5. It is, however, very unlikely that this ratio can be due entirely to differences in the recombination path. In addition (vide infra), comparison of the $^{13}$C-NMR spectra of **7** and **10** unequivocally proves that the main difference in intensities is due to a preferred cleavage of the trimethylbenzoyl moiety.

**$^{13}$C-NMR-CIDNP experiments**. Only information on products stemming from phosphorus-centered radicals is available from $^{31}$P-NMR-CIDNP spectroscopy. Products derived from other radicals can be detected by $^{1}$H-NMR- or $^{13}$C-NMR-CIDNP resonances.

Due to the low natural abundance of the $^{13}$C nucleus, $^{13}$C-NMR-CIDNP experiments are experimentally more difficult to perform than phosphorus or proton spectroscopy. The inherently low sensitivity of $^{13}$C-NMR-CIDNP is partially compensated, however, by the large $^{13}$C hyperfine interactions, which increase the CIDNP enhancement. As an example, the $^{13}$C-NMR-CIDNP spectrum obtained during irradiation of the bisacylphosphine oxide **8** is shown in Figure 7.

$^{13}$C-NMR-CIDNP experiments allowed the detection of escape products from monoacyl- and bisacylphosphine oxides, which are obtained by the combination of two benzoyl radicals. The formation of 2,2′,4,4′,6,6′-hexamethylbenzil (**15**) from the monoacylphosphine oxide **1** and from the bisacylphosphine oxide **5** is shown in Figures 3 and 5, respectively. The same compound, identified by the emission type singlet at 199 ppm

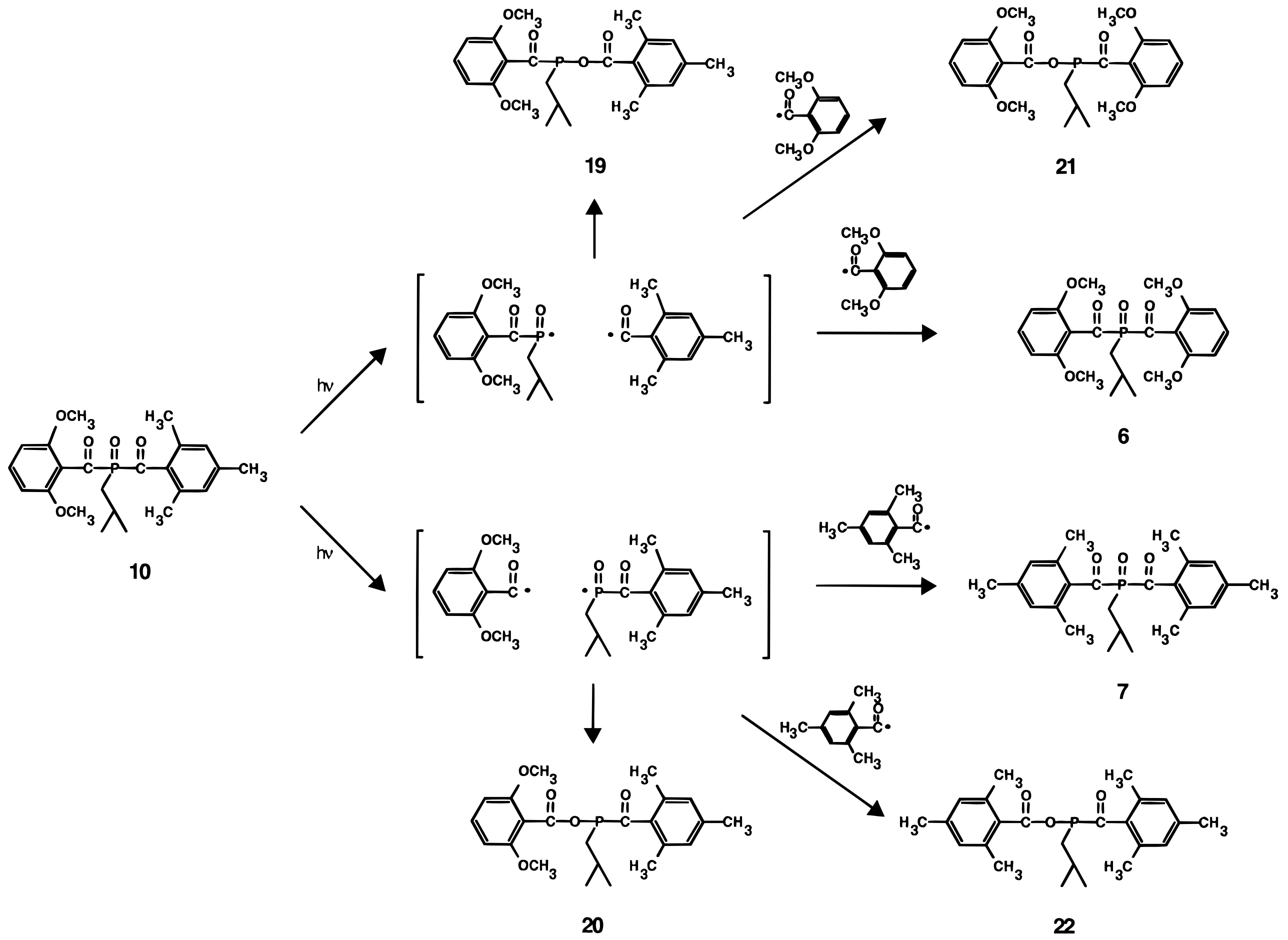


**Figure 6.** Cage recombination and escape products of bisacylphosphine oxide **10** (only phosphorus-containing products are shown).

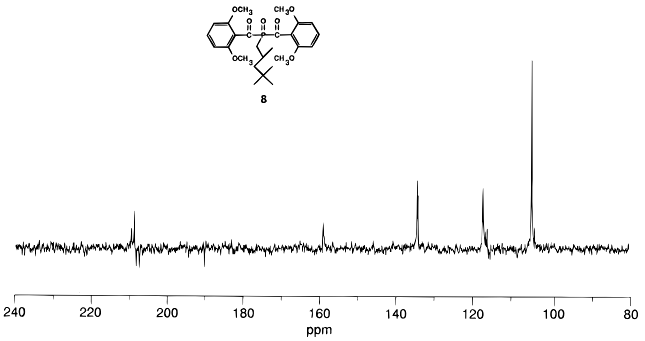


**Figure 7.** $^{13}$C-NMR-CIDNP spectrum of bisacylphosphine oxide **8**.

(carbonyl carbon), is also obtained from the starting materials **3**, **7**, and **9**. 2,2′,6,6′-Tetramethoxybenzil (**23**) (emission type singlet at 191 ppm; see Figure 7) is formed from **2**, **4**, **6**, and **8**. The chemical shifts of both peaks are identical with those obtained from pure **15** and **23**, respectively, isolated via chromatographic purification of product mixtures from preparative irradiation of compounds **1** and **8**.

As discussed above, the modified Kaptein's rules (Table 3) have to be used for the analysis of these $^{13}$C-NMR-CIDNP spectra. Calculation of $\Delta g$ gives

$$\Delta g = g_{\text{carbonyl}} - g_{\text{phosphinoyl}} = 2.0009 - 2.0036 = -0.0027$$

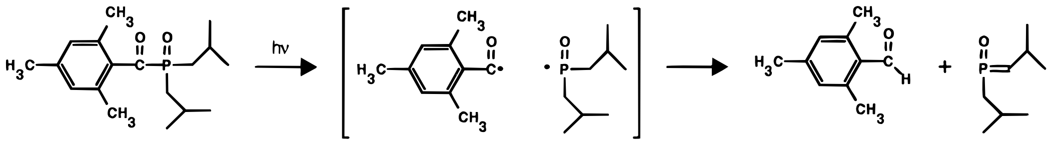
i.e., in Kaptein's rule (eq 1), a negative sign has to be used for $\Delta g$, together with a positive sign for the hyperfine coupling constant of the carbon nucleus, $A_{\mathrm{C}}$,[51] and a negative $\epsilon$ for escape products. A positive $\Gamma_{\mathrm{ne}}$, as required by the modified Kaptein's rules (Table 3) for emission-type polarization, leads once again to the conclusion that the radical precursor must have been a triplet state.

$^{13}$C-CIDNP effects are also observed in the resonances of the carbonyl and of the aromatic C(1) carbons of the starting materials (cage recombination products). These resonances are doublets, exhibiting a net polarization and an A/E multiplet effect. The couplings between the $^{31}$P and the $^{13}$C nuclei were experimentally determined to be in the range of 65−72 Hz ($^{1}J_{\mathrm{C-P}}$ coupling constants) and 36−40 Hz ($^{2}J_{\mathrm{C-P}}$ coupling constants). Analysis of observed polarizations using the appropriate polarization rules results in a positive sign for both coupling constants.

In the $^{13}$C-NMR spectrum of the unsymmetrically substituted bisacylphosphine oxide **10**, the resonances of the carbon atoms of the 2,4,6-trimethylbenzoyl and 2,6-dimethoxybenzoyl moieties can be distinguished. In particular, the absorptions of the carbonyl carbon atoms can be easily identified. These appear as doublets at 217.5 ppm (2,4,6-trimethylbenzoyl) and 210.0 ppm (2,6-dimethoxybenzoyl).

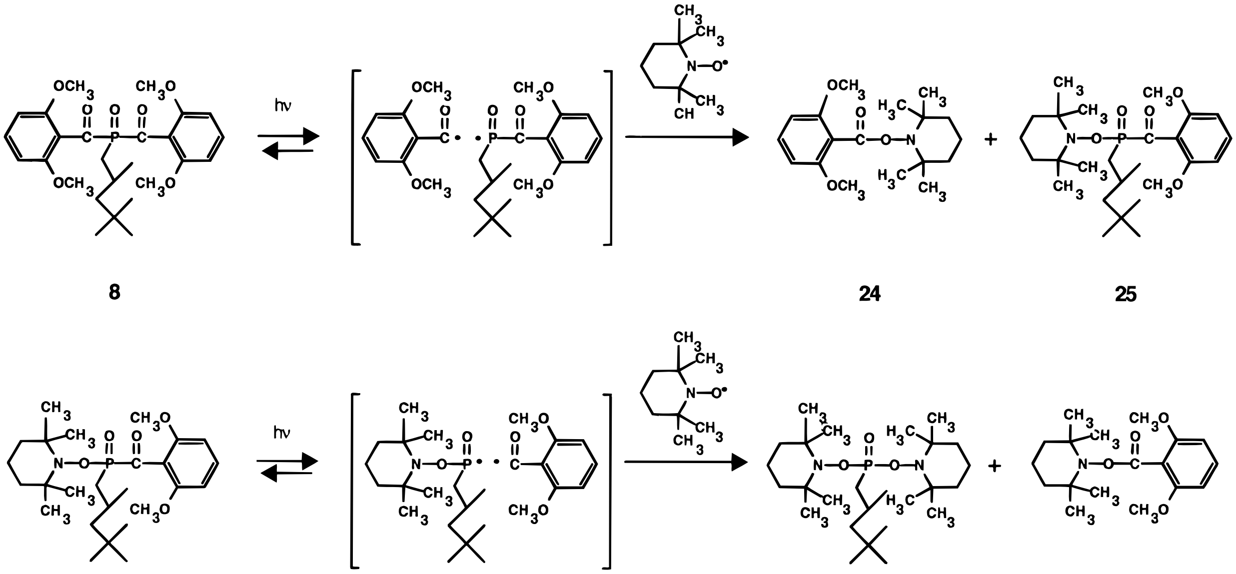
In the $^{13}$C-NMR-CIDNP spectrum obtained from **10**, only the signal at 217.5 ppm shows an A/E multiplet effect, whereas no polarization is observed in the resonance lines at 210 ppm. During the $^{13}$C-CIDNP experiments with compounds **6** and **8** (substituted by 2,6-dimethoxybenzoyl), strong polarization is observed for the carbonyl carbon at 210 ppm. Disregarding steric effects, the above finding indicates that the (2,4,6-trimethylbenzoyl)phosphine oxide is more efficiently cleaved than the (2,6-dimethoxybenzoyl)phosphine oxide.

The emission-type resonance at 199 ppm further confirms the formation of 2,2′,4,4′,6,6′-hexamethylbenzil (**15**), while no



**3**

**Figure 8.** Disproportionation reaction of monoacylphosphine oxide **3**.



**8** **24** **25**

**25** **26** **24**

**Figure 9.** Irradiation of bisacylphosphine oxide **8** in the presence of TMPO: trapping products.

evidence for the formation of 2,2′,6,6′-tetramethoxybenzil (**23**) or an unsymmetric 2,4,6-trimethyl-2′,6′-dimethoxybenzil was found. This is, again, in good agreement with more efficient cleavage of the 2,4,6-trimethylbenzoyl moiety in **10**. It has also been shown in industrial applications that 2,4,6-trimethylbenzoyl derivatives are usually more efficient photoinitiators than their 2,6-dimethoxybenzoyl-substituted counterparts.

**$^1$H-NMR-CIDNP Experiments.** The $^1$H-NMR-CIDNP spectra obtained upon irradiation of each of the monoacylphosphine and bisacylphosphine oxides investigated confirmed the conclusions from the $^{31}$P- and $^{13}$C-NMR-CIDNP spectra. The spectra of compounds **1**, **3**, **5**, **7**, and **9**, bearing the 2,4,6-trimethylbenzoyl group, show a singlet with emission-type polarization at 6.95 ppm, which is assigned to the protons in the 3,3′- and 5,5′-positions in 2,2′,4,4′,6,6′-hexamethylbenzil (**15**). The corresponding protons in 2,2′6,6′-tetramethoxybenzil (**23**) give rise to a doublet at 6.60 ppm with emission-type polarization in the spectra of compounds **2**, **4**, **6**, and **8**.

With the exception of compounds **1** and **5**, which are substituted by a phenyl group on the phosphorus atom, the formation of benzaldehyde derivatives by a disproportionation reaction within the solvent cage could be expected (shown for the monoacylphosphine oxide **3** in Figure 8). This reaction type is well known to occur upon irradiation of many photoinitiators, producing benzoyl radicals.[11,14]

The $^1$H-NMR-CIDNP spectra obtained from the monoacylphosphine oxides **1**−**4** exhibit, however, only very weak signals attributable to benzaldehyde protons. The modified Kaptein's rule requires an emission-type polarization for cage products formed by this disproportionation reaction (positive $\epsilon$ for a cage product, $A_H$ positive,[49] $\Delta g = 0.0027$, and a positive $\mu$ for a triplet precursor). Since only very weak emission lines are observed, this reaction type is, at most, of minor importance for acylphosphine oxide photoinitiators. The primary radicals undergo either in-cage recombination reactions or escape from the solvent cage. Apparently, hydrogen abstraction from the $\beta$-position of the primary phosphorus radicals, such as those shown in Figure 8, is unfavorable. No aldehyde formation was detected for any of the bisacylphosphine oxides investigated.

**Trapping of Primary Radicals from Bisacylphosphine Oxides with TMPO.** 2,2,6,6-Tetramethylpiperidine-1-oxyl (TMPO) is an efficient radical trap for both carbon- and phosphorus-centered radicals. It has proven its utility in the study of the photochemistry of various photoinitiators[11,58,59] as well as for the trapping of phosphinoyl radicals in $^{31}$P-NMR-CIDNP experiments.[36a] Preparative irradiation of bisacylphosphine oxide **8** in acetonitrile in the presence of a 5-fold excess of TMPO resulted in the formation of three products, which were isolated by chromatography. Spectroscopic characterization and microanalysis led to the unambiguous identification of these products as structures **24**−**26** (Figure 9). Compound **24** is the trapping product of the benzoyl radical. It is identical with the compound isolated after irradiation of (2,6-dimethoxybenzoyl)diphenylphosphine oxide in the presence of TMPO.[59] The two novel compounds **25** and **26**, obtained from the phosphorus-centered radicals, were unambiguously identified by their spectroscopical data.

When the same experiment is performed using $^{31}$P-NMR-CIDNP spectroscopy to probe product formation, the development of the reaction with time and the stepwise formation of the two phosphorus radical trapping products can be shown. A series of spectra obtained under the same conditions are shown in Figure 10.

In spectrum a, the strong resonance at 25.35 ppm (enhanced absorption) is the absorption of phosphorus in the starting

---

(58) Hageman, H. J.; Overeem, T. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 719.

(59) Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; Overeem, T. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 311.

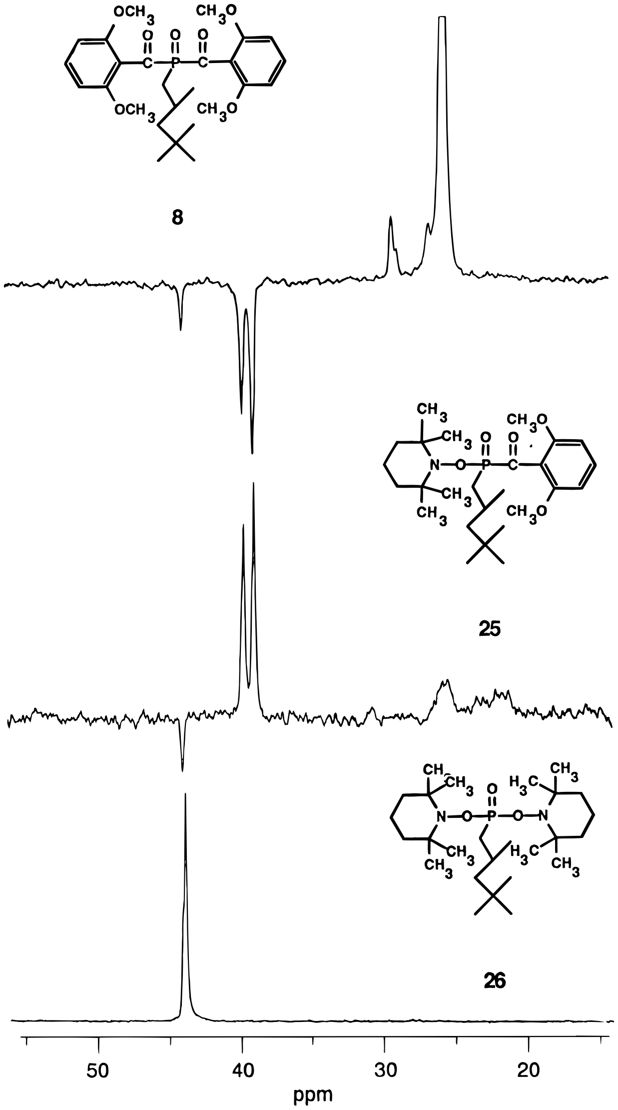


**Figure 10.** Trapping experiments with bisacylphosphine oxide **8** and TMPO: (a) $^{31}$P-NMR-CIDNP spectrum of bisacylphosphine oxide **8** in the presence of TMPO; (b) $^{31}$P-NMR-CIDNP of the trapping product **25** in the presence of TMPO; (c) $^{31}$P-NMR spectrum of the trapping product **26**.

material **8**, formed by an in-cage recombination. The two lines at 38.73 and 39.49 ppm, carrying emission-type polarization, are attributed to the TMPO trapping product **25** of the primary phosphinoyl radical. The product is formed as a mixture of diastereomers, since in addition to the asymmetric center in the alkyl chain, a second asymmetric center is formed on phosphorus by the trapping reaction.

Compound **25** is a monoacylphosphine oxide and is therefore able to undergo a second photoinduced cleavage reaction. Indeed, a new resonance is observed in the $^{31}$P spectrum at 46.65 ppm (emission-type polarization, Figure 10, spectrum a), which is not present after short irradiation times. This resonance is also found when compound **25** is irradiated under the same conditions in the presence of an excess of TMPO (Figure 10, spectrum b). The two signals of compound **25** carry positive polarization in this spectrum, since **25** is formed as a cage recombination product under these conditions.

The resonance at 46.65 ppm must be attributed to the second trapping product **26**, as shown by comparison with the $^{31}$P-NMR spectrum of the isolated compound (Figure 10, spectrum c). Those findings prove that **8** undergoes a stepwise cleavage of the two benzoyl moieties, affording two substituted benzoyl radicals and two phosphorus-centered radicals. These radicals are all capable to initiate radical polymerization reactions.

The same photochemical reaction sequence was found to occur with the other bisacylphosphine oxides investigated. When the unsymmetrically substituted bisacylphosphine oxide **10** is studied under the same conditions, the polarized resonance of the trapping product obtained from the (2,6-dimethoxybenzoyl)-2-(methylpropyl)phosphinoyl radical is more intense than that of its 2,4,6-trimethylbenzoyl-substituted counterpart. In agreement with the results obtained from $^{31}$P-NMR-CIDNP and $^{13}$C-NMR-CIDNP spectroscopies, this experimental finding can be explained either by a more efficient photochemical cleavage of the 2,4,6-trimethylbenzoyl part of the molecule or by a more efficient reaction of the 2,4,6-trimethylbenzoyl radical with TMPO. However, since steric effects of the *ortho* substituents on the reactivity of the benzoyl radical should influence both the trapping and the recombination reaction, more efficient cleavage seems more likely.

**Trapping of Primary Radicals by Methyl 2-*tert*-Butylacrylate.** The initiation process of an acrylate polymerization can be studied using methyl 2-*tert*-butylacrylate (**27**) as a trapping agent. While the addition of an initiating radical to the 3-position of the acryate can easily occur, further reactions of the resulting radical in the 2-position are rendered difficult by the high steric bulk of the *tert*-butyl group. Hydrogen abstraction is, therefore, preferred over chain propagation, and the product of a simple addition reaction can be isolated. This provides information on the reactivity of the primary radicals toward acrylic double bonds.[11] The radicals **28** and **29** formed by irradiation of monoacylphosphine oxide **3** in the presence of excess methyl 2-*tert*-butylacrylate are shown in Figure 11.

The ESR spectrum recorded during continuous irradiation of compound **3** in the presence of a 20-fold excess of methyl 2-*tert*-butylacrylate (**27**) in toluene is shown in Figure 12. The addition product of the phosphinoyl radical gives rise to doublets of four lines. The hyperfine splitting of 6.5 mT is due to the coupling with the phosphorus nucleus, while smaller couplings of 1.5 and 1.1 mT are attributed to the coupling with the protons on the methylene group. The addition product of the benzoyl radical is detected in the center of the spectrum shown in Figure 12. It consists of a doublet of doublets with hyperfine couplings of 1.3 and 0.8 mT, due to the methylene protons. A small coupling (about 0.07 mT) from the protons of the *tert*-butyl group is also resolved.

Similar ESR experiments have been run at room temperature with bisacylphosphine oxides and methyl 2-*tert*-butylacrylate. While the spectra obtained are similar to those of monoacylphosphine oxides, the analysis is more difficult due to the occurrence of a second photoreaction of the phosphinoyl addition product.

When the analogous experiments are performed at 180−220 K, only the resonances of the phosphinoyl radical addition product, together with the resonance of the unreacted benzoyl radical, are observed at the beginning of the irradiation. This is clear evidence that the addition of the phosphorus radicals obtained from bisacylphosphine oxides to the acrylate double bond is more efficient than that of the benzoyl radical. This finding is in good agreement with results obtained for monoacylphosphine oxides by other techniques, which indicate that phosphinoyl radicals are 1−2 orders of magnitude more reactive than the benzoyl radical toward unsaturated substrates.[18,25−28] Further ESR studies of the reaction of bisacylphosphine oxides are underway.

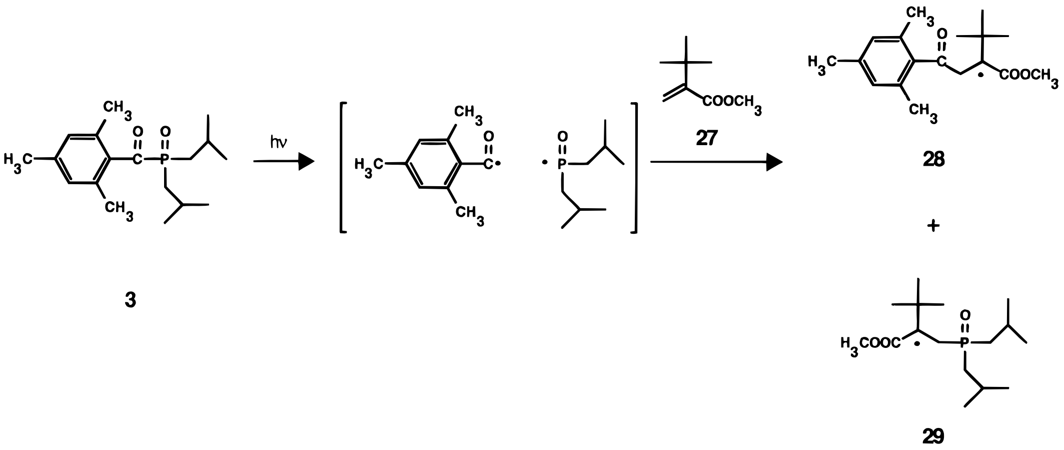


**Figure 11.** Addition of the primary radicals of monoacylphosphine oxide **3** to methyl 2-*tert*-butylacrylate.

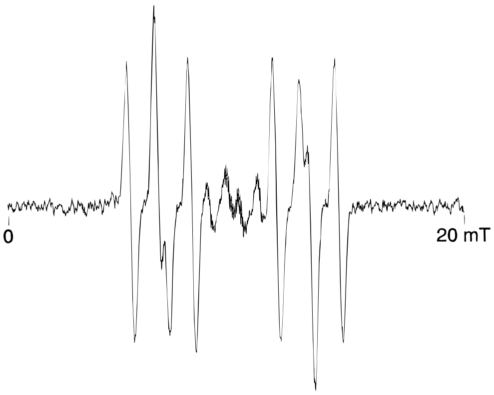


**Figure 12.** ESR spectrum of the radicals **28** and **29**.

## Conclusion

The photochemistry of four monoacylphosphine oxides and six bisacylphosphine oxides, which are efficient photoinitiators for radical polymerization, was investigated using CIDNP and ESR techniques. $^{31}$P-NMR-CIDNP spectroscopy was applied for the first time to the investigation of photoinitiators and proved to be a powerful tool for the study of the phosphorus-containing products.

A modified Kaptein's rule, which takes the large hyperfine coupling constant of the $^{31}$P-nucleus into consideration, had to be used for the interpretation of the $^{13}$C and $^{1}$H spectra. Using these rules, analysis of the spectra obtained from $^{31}$P-, $^{13}$C-, and $^{1}$H-NMR-CIDNP experiments gave consistent results. Thus, all compounds were unambiguously shown to undergo a photoinduced cleavage of the carbonyl−phosphinoyl bond from a triplet state precursor.

The primary radicals can undergo various reactions. Since the phosphinoyl radicals possess sufficient spin density both at the phosphorus and at the oxygen atoms, reactions at both centers occur, yielding both P−O and P−P dimers. The phosphinoyl radicals derived from bisacylphosphine oxide precursors are substituted by a benzoyl group, and hence a further delocalization of spin density onto the benzoyl oxygen atom is proposed to explain some of the product resonances detected in the $^{31}$P spectra.

Analysis of the polarization pattern of products containing two phosphorus atoms allowed the determination of the sign of the $^{2}J_{P-P}$ coupling constants. This in turn provided information on the conformation of the partial structure involving the coupled nuclei. Thus, the *cisoid* arrangement of the phosphorus(V)−oxygen bond and the phosphorus(III) lone pair in most of the phosphinous phosphinic acid anhydride derivatives could be established.

Weak signals of benzaldehyde derivatives, formed by a disproportionation reaction of the primary radicals, were detected for some of the initiators. The low efficiency of this reaction, which is important in the photochemistry of other α-cleavage-type photoinitiators, results in higher photoinitiator activity since less initiating radicals are consumed in wasteful processes.

Bisacylphosphine oxides undergo stepwise cleavage of both benzoyl residues. This was shown by the use of trapping agents, whereby the intermediate product obtained after the first photoreaction could be isolated. When photoinitiators possessing an asymmetric center in the side chain are used, the products formed in the stepwise process are easily identified, not only by the chemical shifts of the products but also by the number of resonance lines. The latter reflect the formation of different diastereomers.

ESR experiments in the presence of a model acrylate led to the characterization of the adduct resulting from the addition of primary radicals to an acrylic double bond. It could be clearly shown that phosphorus-centered radicals are more active than their benzoyl counterparts.

The results obtained serve to further elucidate the photochemistry of monoacylphosphine oxides and establish an analogous, stepwise reaction for the new class of bifunctional bisacylphosphine oxide photoinitiators. In addition, important differences between these compounds and other type I photoinitiators were revealed, which should lead to a better understanding of the technically important curing properties of phosphorus-containing photoinitiators.

**Acknowledgment.** This paper is part of the Ph.D. thesis of U.K. We acknowledge the management of Ciba-Geigy Ltd. for the permission to publish this study.

**Supporting Information Available:** Spectroscopic and analytical data of mono- and bisacylphosphine oxides **2**−**10** and of the photoproducts **23**, **25**, and **26** (4 pages). Ordering information is given on any current masthead page.

JA9534213