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SYNTHESIS AND CHARACTERIZATION OF
ACYLPHOSPHINE OXIDE PHOTOINITIATORS

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SYNTHESIS AND CHARACTERIZATION OF
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HANY F. SOBHI

ABSTRACT

Recently, polymerization science has assumed an increasing relevance in many applications, including orthopedic and dental biomaterials. Current technologies are based on the use of photochemically reactive systems, which are suited to absorb light to produce primary radical species capable of initiating polymerization. Acylphosphine oxides and acylphosphonates are known to be very effective photoinitiators for various unsaturated polymeric systems. The high reactivity observed was ascribed to the phosphinyl and phosphinoyl radicals generated. Because of the poor qualities of other initiators, we examined new routes to synthesize acylphosphine oxide initiators to achieve compatibility with aqueous media and improved performance. The preparation and spectroscopic characterization of a series of compounds, including acylphosphine oxides and bisacylphosphine oxides, are fully reported for the first time. These types of initiators have potential application in a variety of biomedical uses, with the promise of low toxicity and innocuous incorporation into organic matrices and tissues.
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CHAPTER I

INTRODUCTION

1.1 GENERAL BACKGROUND

The increase in human life expectancy has produced an increasing demand for biomaterials. In recent years, new biomaterial have been developed through object-oriented synthesis, blends, and modifications that produce tailor-made characteristics for the areas where these materials will be used. The two most important requirements for biomaterials in their numerous operational areas are biofunctionality and biocompatibility, defined as the ability of the biopolymer material to perform with an appropriate host response in specific applications. In most cases, the functionality is satisfied through the various mechanical characteristics of currently available materials. Due to the high production standards in material engineering, it is now possible to produce high quality products of suitable design. Nevertheless, these products must retain their functions in an aggressive environment effectively and safely over the desired period of time (at least ten to fifteen years) without irritation of the surrounding tissue by either mechanical action or possible degradation products which can be ensured only with biocompatible materials.
Only a better understanding of the interaction between biomaterials and biosystems will lead to development of suitable polymeric biomaterials and the successful use of the implants.\textsuperscript{3}

Tissue engineering scaffolds based upon the biodegradable polyester polypropylene fumerate (PPF) have been produced using a photocrosslinking/porogen leaching strategy. PPF was crosslinked with long wavelength UV light (> 350 Å) using the initiator \textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine oxide. Porous scaffolds were formed by photocrosslinking PPF around a NaCl porogen, which was then removed by water leaching. An examination of the \textit{in vitro} degradation of the porous PPF scaffolds in buffer saline showed a decrease in elastic modulus and increase in water absorption and increase in porosity attributable to porogen removal; after porogen removal, the porous scaffolds showed a relatively constant elastic modulus, water absorption, and porosity while a slight decrease in the scaffolds mass and length was exhibited. These results demonstrated the feasibility of forming biodegradable tissue scaffolds by a photocrosslinking, porogen-leaching technique.\textsuperscript{4,5}

\subsection*{1.2 PHOTOINITIATED POLYMERIZATION OF BIOMATERIALS}

Many investigations into photoinitiated materials have explored strategies to create biomaterials that attempt to replace lost function or to add a new function. Examples of the former include dental and cardiovascular materials, and the later include drug delivery systems and biological adhesives. Photochemistry is an attractive strategy in the production of these materials because of the controlled initiation and termination, and often short reaction times and special controls are
possible. Biomedical polymers made by the photopolymerization of multifunctional acrylates and methacrylates are of interest for use as dental biomaterials. For example, photopolymerized multifunctional methacrylates were prepared and used as model polymers for dental applications.

1.3 PHOTOINITIATION AND PHOTOCROSSLINKING

Photochemistry is a method which can promote specific bonds to crosslink. Furthermore, light-induced polymerization is the basis of important advanced technologies, since it is among the most efficient methods capable to achieve fast and extensive curing of multifunctional oligomers. Highly reactive systems are cured within a fraction of a second upon exposure to intense UV radiation or laser beams, transforming a liquid resin into a strongly cross-linked polymer without the need of additional heat. Biological adhesives and scaffolds have been prepared by the introduction of conventional functional groups, which can be crosslinked photochemically into natural and synthetic polymers. For example, photolabile azide groups have been incorporated into commercially-available chitosan and the polymer crosslinked by brief exposure to ultraviolet light (254 nm). However, the use of such photolabile groups suffers a number of disadvantages, including difficult synthesis and the participation of the photolabile groups in side reactions.

Another method involves the use of external chemical initiators and sensitizers to crosslink an unsaturated polymer or a polymer to which alkenyl groups have been chemically attached. Examples of such polymers are poly(ethylene glycol) fumarate and polypropylene fumarate PPF, which were crosslinked...
photochemically to form porous scaffolds for backbone tissue engineering applications. PPF was crosslinked using the photoinitiator \textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) and exposure to 30 minutes of long-wavelength ultraviolet light.\textsuperscript{15} Poly(ethylene glycol) acrolate, fumarate, and cinnamate are easily prepared, producing a wide range of crosslinkable groups.\textsuperscript{16}

Photochemical initiators are commonly used for crosslinking unsaturated monomers and polymers containing unsaturated functional groups. These initiators typically absorb light in the far UV region and act by homolysis to form organic radicals. The radicals initiate crosslinking of alkenes by radical addition processes. A number of issues must be considered when choosing a photoinitiator for polymerization of biomaterials as described below. Such concerns are not limited to the photoinitiators but extend to the interaction between the available light source and other chemical species within the implant production system. The maximum absorption wavelength, the extinction coefficient of the photoinitiator, the reactivity of the initiator towards the other species within the system, and finally the kinetics of the photoinitiators, all determine the applicability of the system. Examples of such photoinitiators include organoperoxides (ROOR), which absorb in the region from 200 to 300 nm and react by cleavage of the O-O bond to form alkoxy radicals (RO.). Hydroxyl radicals (HO\textsuperscript{•}) formed from hydrogen peroxide similarly have been used to polymerize methyl methacrylates. Benzoyl peroxide (C\textsubscript{6}H\textsubscript{5}CO\textsubscript{2})\textsubscript{2} is a common thermal radical initiator which absorbs at 230 and 273 nm. Ketones (RCOR) such as acetophenone (C\textsubscript{6}H\textsubscript{5}-CO-CH\textsubscript{3}), which has a large absorbance peak at 280 nm and a smaller peak at 330 nm, form benzoyl radicals (C\textsubscript{6}H\textsubscript{5}-CO\textsuperscript{'}) after \(\alpha\)-cleavage of the C-
CH₃ bond. Benzoin (C₆H₅-CHOH-COC₆H₅) which absorbs at 315 nm has been similarly employed, and another common initiator is 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, Ciba-Geigy), which enhances radical polymerization because of its electron donating substituents and its ability to undergo a secondary excitation and reactions. The primary reaction a photochemical α-cleavage from a short-lived triplet state (τₜ < 100 ps). The result is a more potent initiator because three different radical fragments can be produced (Figure 1).

\[
\begin{align*}
\text{OMe} & \quad \text{C} & \quad \text{O} \\
\quad & \quad \text{OMe} \\
\text{OMe} & \quad \text{C} & \quad \text{O} \\
\quad & \quad \text{OMe} \\
\quad & \quad \text{OMe} \\
\quad & \quad \text{OMe} & \quad \text{C} \\
\quad & \quad \text{OMe} & \quad \text{O} \\
\quad & \quad \text{Me.} & \quad \text{h} \nu
\end{align*}
\]

(1)

**Figure 1.** Photochemical α-cleavage of 2,2-dimethoxy-2-phenylacetophenone

The free radical reactions induced by the photocleavage of the photocuring agent 2,2-dimethoxy-2-phenylacetophenone were studied by product analysis, CIDNP, and by optical and ESR spectroscopy. These techniques showed that the photochemistry of these compounds are strongly influenced by both thermal and photochemical fragmentation of the α,α-dimethoxybenzyl radical.

Polysiloxane photoinitiators have been synthesized and the photopolymerization rates for methyl methacrylates were studied. The pulse transient absorption
spectra of these photoinitiators on the microsecond time scale using flash photolysis were assigned to the benzoyl radical produced on direct photolysis of the acetophenone chromophores. The transient absorption spectra were also correlated with the photopolymerization rates of methyl methacrylates, indicating that the benzoyl radical is the key initiating species. This assignment was confirmed by the identification of benzaldehyde in the photolysis products of polysiloxanes on repetitive flash photolysis in THF, where benzoyl radicals abstract a hydrogen from the solvent. The second order derivative absorption analysis of the poly(methyl methacrylates) confirms the involvement of the benzoyl radical as the active chain initiator.21

Azo compounds have found use as photoinitiators, as the azo group (-N=N-) absorbs at approximately 350 nm to produce two reactive carbon-centered radicals after loss of N₂. For example, 2,2-azo-bis-isobutyronitrile [(CH₃)₂C(CN)-N=N-C(CN)CH₃] has been used; however, the low absorptivity and associated low polymerization rate are chief disadvantages of azo compounds.17

The reactivity of benzoyldiphenylphosphine oxides, benzoylphosphonates, and pivaloylphosphonates as photoinitiators in free radical vinyl polymerization process was studied at 347 nm, in which α-scission occurs upon irradiation to give the phosphinoyl radical and the acyl radical. The quantum yield of the reaction depends on the nature and the chemical structure of the acyl group of the initiator. Benzoylphosphonates produced a very small quantum yield and the major route of the deactivation of electronically excited phosphonates involves the intersystem crossing to the triplet manifold.18
Acylphosphine oxides \( [C_6H_5COPO(C_6H_5)_2] \) have been used as photoinitiators in the photocrosslinking of PPF to form porous scaffolds for bone tissue engineering and dental applications. Diacylphosphine oxides are highly efficient photoinitiators. These materials strongly absorb in the near UV to the visible region of the spectrum and have been shown to photolize in a stepwise fashion to produce up to four radicals (Figure 2). \(^\text{22}\)

![Figure 2. α-Cleavage of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide](image)

The reaction of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, available commercially as Irgacure 819, with methyl 2-\textit{tert}-butylacrylate has indicated that the cleavage produces both phosphorus- and carbon-centered radicals. Electron spin resonance ESR also showed that the addition of the phosphorus centered radicals to
the acrylate bond was more efficient by at least one order of magnitude than that of trimethylbenzoyl radicals (Figure 3).²³

![Diagram of Irgacure 819](image)

**Figure 3.** Synthesis of macrophotoinitiator

Irgacure 819 also was used as photoinitiator in the preparation of polymers with photoactive end groups that were in turn used to prepare block copolymers (Figure 4). As a result of the initiation reactions involving either the parent initiators or the polymers derived from them, polymers with phosphorus-containing end groups or block junctions were formed.²² Photoinitiated radical chain polymerization begins with light irradiation of a properly sensitive compound typically fragments into two
radicals that attacks a monomer, converting it to a radical, which attacks a second monomer and this process continues, thereby forming the polymer.

Figure 4. Synthesis of block copolymer
1.4 BIODEGRADABLE PHOTOPOLYMERS FOR BONE TISSUE ENGINEERING

Photopolymerized materials have been extensively used in various orthopaedic methods for the fixation of fractured bone and dental applications because they possess advantageous properties such as low shrinkage, low water absorption and good adhesion. A typical photoinitiator dental material is comprised of four elements: a monomer, a diluent, a photoinitiator, and inorganic filler. Biodegradable polyester polymers such as poly(glycolic acid) and poly(lactic acid) had been used and serve quit well for the fixation of fractured bones but it is only limited to small bone repairs, and can not be used in the case of large defects, for example after the removal of bone tumors because of their hydrolytic degradation which causes fast loss in mechanical strength. Moreover, the locally high concentration of the free acids can result in tissue necrosis.

1.5 THE USE OF ORGANIC COMPOUNDS OF PHOSPHORUS IN CLINICAL DENTISTRY

Phosphorus forms compounds in which it shows valencies of three and five; in terms of abundance it is the eleventh most common element in the earth crust. Phosphorus is capable of forming true organophosphorus compounds which contains C-P bond. Such bond formed from overlapping s-type orbitals are $\sigma$ in nature, and in general are stable with respect to thermal decomposition and hydrolysis at room temperature. These compounds have been prepared for use as nerve gases in chemical warfare, typically they have two effects, inhibition of cholinesterase
following transmission of a nerve impulse and delayed neurotherapy. The aesthetic filling materials most widely used in modern dentistry are so called composite resins. The major disadvantage of composite resins is their lack of adhesion to dentine. A number of organic compounds of phosphorus have been considered for use as bonding agents, the very first dentine bonding agent was developed by Hagger in the early 1950s. This was based on glycerol/phosphoric acid/dimethacrylate and sold under the name of Sevriton Cavity Seal and it has a nonpolar tail and strongly polar head. Several monomers containing the phosphonic acid functional group have been prepared and tested for use, for example as comonomer capable of aiding adhesion of the resulting polymer. The vinyl phosphonic acid and vinylbenzyl phosphonic acid monomers exhibit significant adhesion and proved to be persistent when subjected to immersion in water. Incorporation of these monomers into the acrylic monomer results in the formation of a new polymer that showed strong adhesion to dental enamel.

1.6 FLUORINATED PHENYLPHOSPHINE OXIDE POLYMERS FOR POTENTIAL SPACE APPLICATIONS

Polymers containing phenylphosphine oxide (PPO) have been extensively studied for a number of applications. McGrath et al had reported the synthesis and excellent flame retardant properties of aromatic polyphosphonates. Other examples of polymers containing PPO moiety include metal complexation, coatings, and membranes for space application due to their notable feature of atomic oxygen resistance. Phenylphosphine oxide has been incorporated into the backbone of
pentafluorocyclobutyl (PFCB) polymers, and were prepared by using the well-established intermediate strategy of delivering the trifluorovinyl aryl ether via Grignard or aryllithium chemistry. Photopolymerization of *bis*- and *tris*-trifluorovinyl ether monomers were carried out in the bulk above 200° C as shown in Figure 5.

![Chemical Structures](image.png)

**Figure 5.** The bulk polymerization of *bis*- and *tris*-trifluorovinyl ether monomers with phenylphosphine oxides.

Thermal analysis by DSC found these polymers to be amorphous with no crystalline transition temperature, and the initial stimulated space environment evaluation has been performed at NASA Marshall reported. The most prevalent
atmospheric species in low earth orbit (LEO) between the altitude of 180 and 650 km is atomic oxygen which was formed by photodissociation of upper atmospheric oxygen by short wave length UV radiation. The atomic oxygen is very reactive and vigorously erodes organic polymers if they are unprotected. After exposure to atomic oxygen for four month in LEO, a PFCB copolymers containing 12.5 wt % of PPO had lost only 2% of its total mass versus 33% of the PFCB with out PPO.38

1.7 RECENT DEVELOPMENT IN PHOSPHINOYL RADICAL PHOTOINITIATORS

Reactions of phosphorus- and carbon-centered radicals are key steps in biological transformations, organic synthesis and polymer chemistry. A typical example is the addition of these reactive species to alkenes. An efficient method for the controlled formation of radicals is to generate them by a photochemical reaction from a photoinitiator designed for this purpose.39 The reactivity of benzoyldiphenyl phosphine oxides, benzoylphosphonates, and pivaloylphosphonates as photoinitiators in free radical vinyl polymerization process was studied at 347 nm, in which α-scission occurs upon irradiation to give the phosphinoyl radical and the acyl radical. The quantum yield of the reaction depends on the nature and the chemical structure of the acyl group of the initiator. Benzoylphosphonates produced a very small quantum yield and the major route of the deactivation of electronically excited phosphonates involves the intersystem crossing to the triplet manifold.18 Acylphosphine oxides [C₆H₅COPO(C₆H₅)₂] have been used as photoinitiators in the photocrosslinking of PPF to form porous scaffolds for bone tissue engineering and dental applications.16
Diacylphosphine oxides are highly efficient photoinitiators. These materials strongly absorb in the near UV to the visible region of the spectrum and have been shown to photolize in a stepwise fashion to produce up to four radicals (Figure 2).\(^{40}\)

The reaction of \textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine oxide,\(^{41}\) available commercially as Irgacure-819, with methyl 2-\textit{tert}-butylacrylate has indicated that the cleavage produces both phosphorus- and carbon-centered radicals. The electron spin resonance ESR also showed that the addition of the phosphorus centered radicals to the acrylate bond was more efficient by at least one order of magnitude than that of trimethylbenzoyl radicals (Figure 3).\(^{23}\)

Diacylphosphine oxides and acylphosphonates have been used as bifunctional photoinitiators for block copolymer synthesis of styrene and showed a significant advantage over azobenzoin initiators regarding their use in block copolymer synthesis, since UV irradiation of the benzoin terminated pre-polymers obtained by azobenzoin initiators yields polymer bound alkoxybenzyl radicals and benzoyl radicals. Because of the similar reactivity of both radicals towards vinyl monomers homopolymer formation arising from the low molar mass benzoyl radicals is unavoidable. In case of diacylphosphine oxides the homopolymer formation can be minimized by taking advantage of the long wavelength absorption and the high reactivity of the phosphinoyl radicals, which in turn make these initiators particularly useful for the polymerization of TiO\(_2\) pigmented formulation containing acrylate or styrene type monomers and of glass fiber reinforced polyesters laminates with reduced transparency.\(^{42,43}\) Structurally, terminal acylphosphine oxides moieties mimic TMDPO photoinitiator. Thus, upon irradiation of the resultant polymer at $\lambda =$
380 nm produces polymeric phosphonyl radicals and lower molar mass benzoyl radicals. In the presence of a secondary monomer such as MMA faster initiation with the phosphonyl radicals afforded the formation of block copolymers as explained in Figure 2.

**Figure 6.** The photodecomposition of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (1) in the presence of 1,1-di-p-tolylethylene
Figure 6 (continued). The photodecomposition of (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide (1) in the presence of 1,1-di-p-tolylethylene (DTE) (R¹ = mesitoyl)
The photodecomposition of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (1) in solution at 40° C was studied in a nitrogen atmosphere in the presence of 1,1-di-p-tolylethylene as a model substrate for vinyl monomers as explained in Figure 6. Both primary radicals resulting from α-cleavage of (1) were found to add to olefinic double bond of the substrate (initiation). The diphenylphosphinoyl radical (3) proved to be twice as effective as the 2,4,6-trimethylbenzoyl radical (2) under all conditions (Figure 6).\textsuperscript{40}

\begin{align*}
\text{Benzoic acid} & \quad \text{Thionyl Chloride} & \quad \text{Benzoyl Chloride} \\
\text{Benzoyl Chloride} & \quad \text{Triethyl Phosphite} & \quad \text{Diethyl benzoylphosphonate} \\
\end{align*}

\textbf{Figure 7.} Synthesis of diethyl benzoylphosphonate.\textsuperscript{44,4}
Polyphosphonates were shown to have pronounced anti carcinogenic activity and non toxicity and was employed from time to time as ingredients for dental applications.\textsuperscript{47} Diethyl benzoylphosphonate photoinitiator has been synthesized according to the reaction in explained in Figure 7.\textsuperscript{44, 45, 46}

The photolysis and stability in aqueous medium were investigated, and the reaction mechanism of the hydrolysis was found to be Cope type elimination Figure 8, i.e. pseudo first-order in the substrate,\textsuperscript{44} the chief disadvantage of these initiators is that it undergoes hydrolysis in aqueous and acidic media, which in turn make it less compatible for dental application.

The influence of the alkyl substitution in benzoyldiphenylphosphine oxides was investigated\textsuperscript{48} and it showed that upon irradiation of the phosphine oxides in argon saturated dichloromethane solution with flashes (20 ns at 347 nm) transient difference spectra in the wavelength range between 300 and 450 nm specifically at $\lambda = 335$ nm were observed, which was assigned to phosphinoyl radicals (Ph)$_2$P•=O.\textsuperscript{10} Oxygen did not affect the formation of the transient absorption but strongly accelerated its decay.\textsuperscript{49} The substitution of hydrogen at the benzoyl group by methyl groups only has a drastic effect in the case of \textit{para} substitution which was cleaved twice as effectively as the non-substituted phosphine oxides. The trimethyl-substituted compound undergoes $\alpha$ scission with the same yield as the non substituted compound indicating that the three methyl groups do not exert any influence on $\alpha$ scission. The different behavior in the presence and absence of the methyl substitution was discussed in term of its ground state conformation being unfavorable to the
Figure 8. Proposed Cope-type elimination for the hydrolysis of diethyl benzoylphosphonate.\textsuperscript{44}
interaction of the carbonyl group with the ortho methyl group. It was reported that photoenolization was not observed with (2,4,6-trimethylbenzoyl)diphenylphosphine oxide which possesses methyl groups in the ortho position, whereas it was detected with diethyl (2,4,6-trimethylbenzoyl)phosphonate that different in behavior correlated with the lifetime of the ketone triplets which is very short (0.3 ns) in case of the phosphine oxide and substantially longer (more than 3.0 ns) in case of the phosphonates.\textsuperscript{50} It is also pertinent to note that (2,4,6-trimethylphenyl)alkyl ketones are known to be highly twisted in their ground states,\textsuperscript{51} therefore the present of a second methyl group in the ortho position to the carbonyl produces a conformation with the carbonyl in a position perpendicular to the trimethyl phenyl moiety, and the interactions of the excited carbonyl with the ortho methyl groups are strongly impeded. Evidence for this steric effect comes from the ground state spectra which show a slight blue shift of the $\pi^* \leftarrow n$ absorption. This steric hindrance effect had a great influence in the stability of these compounds for their use in formulations.\textsuperscript{49}

1.8 REACTION MECHANISM OF ACYL- AND DIACYL-PHOSPHINE OXIDES PHOTOINITIATORS STUDIED BY $^{31}$P-CIDNP

A number of methods for the investigation of short-lived reactive intermediates in solutions have been developed in the last decade; many of them are based on the influence of resonance microwave and radiofrequency fields on nuclear polarization of diamagnetic products. Stimulated nuclear polarization (SNP), dynamic nuclear polarization (DNP), and nuclear magnetic resonance (NMR)-detected nuclear resonance of transient radicals (NMR-NR) are examples of such
techniques.\textsuperscript{52} SNP spectroscopy originates through the influence of an mw fields on the rate of singlet to triplet conversion in radical pairs.\textsuperscript{53} DNP is formed due to the cross relaxation processes which transfer non-Boltzmann electron polarization created by resonance with an mw field into nuclear polarization of the intermediate free radicals.\textsuperscript{54} Also, NMR-NR detects rf–driven transition between hyperfine states in transient radicals.\textsuperscript{55,56} Electron- nuclear spin transition in short-lived phosphonyl radicals have been investigated \textit{via} chemically induced dynamic nuclear polarization technique (CIDNP).\textsuperscript{57} \textsuperscript{31}P- NMR CIDNP spectroscopy was applied to investigate the formation and reaction of phosphorus–centered radicals obtained from phosphorus containing photoinitiators. In these studies four monoacylphosphine oxides and six diacylphosphine oxides were used. All four 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 due to the resonance structure between phosphorus and oxygen atoms (Figure 9), reactions at both centers occurs, yielding both P-O and P-P dimers.\textsuperscript{22}

\begin{center}
\begin{tabular}{c}
\textbf{Figure 9.} Resonance structure of phosphinoyl radicals
\end{tabular}
\end{center}
The spin density distribution in the phosphinoyl radicals suggested that three possible types of escape products may be obtained by recombination of these radicals (Figure 10). The formation of the dimer with a P-P bond and that with a P-O bond was observed in the $^{31}$P-CIDNP spectrum obtained, and there were no evidence of the formation of O-O recombination products.

Figure 10. Escape products from recombination of phosphinoyl radicals
1.9 $^{31}$P NMR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

1.9.1 GENERAL HISTORY

The phosphorus atom plays a central role in the chemistry of most compounds in which it is incorporated. It has been of paramount importance to follow and understand the changes in bonding and stereochemistry that occur at phosphorus. After 1950, chemists interested in phosphorus compounds (some of which were produced industrially and were exhibiting phenomenal market growth) began to utilize the ideas and techniques of polymer science, chemical physics, and advanced organic chemistry. Since many phosphorus compounds were quite labile compared to the compounds of classical organic chemistry, they easily undergo rearrangements and other reactions. Gentle methods were needed for identifying what compounds initially resulted from a particular chemical reaction. Thus the newly developing physical procedures for the nondestructive analysis of molecules in a mixture were of special value (particularly paper and column chromatography and $^{31}$P NMR). Nuclear magnetic resonance involving nuclear spins of $\frac{1}{2}$ afforded a chemically non-perturbing differentiation of the various intermolecular environments of all the atoms containing the active nucleus in a fluid. The $^{31}$P nucleus, with spin $\frac{1}{2}$, exhibits a relatively high NMR sensitivity, due to 100% natural abundance, relatively large magnetogyric ratio, and large chemical shift range. Shortly it becomes the method of choice for rapid molecular assays for phosphorus chemists who could afford a multinuclear NMR spectrometer. By 1960, the use of NMR based on $^{31}$P and other
nuclei (particularly $^1$H) for the determination and characterization of phosphorus compounds was well established and effort was being directed to the study of rapid reactions using NMR line broadening. In 1967, enormous progress was been made because of the introduction of Fourier transform (FT) techniques for acquiring $^{31}$P NMR data.

By 1970, $^{31}$P NMR spectroscopy had become a primary experimental technique in many areas organic compounds, coordination chemistry and biological systems. By 1983, instrumental and relaxation aids available to enhance sensitivity made it possible to estimate phosphorus compounds at the 200-level down to even the 5-ppm level. This capability has been put to rapid use in the biological fields, since the phosphorus atom is involved directly in many vital biochemical reactions.\textsuperscript{58}

1.9.2 CHEMICAL SHIFTS

Phosphorus chemical shifts extend over a range exceeding 1000 ppm. The presence of a lone pair of electrons on the phosphorus tends to widen the chemical shift range. $^{31}$P chemical shifts usually are reported relative to the signal for 85% phosphoric acid. The acid is invariably used as an external reference due to its reactivity. A number of secondary standards are in use that gives much sharper signals than 85% phosphoric acid. A 0.2 M solution of crystalline phosphoric acid in 14% aqueous perchloric acid (tetrahydroxyphosphonium perchlorate) gives a very sharp signal at $\delta -0.0667$ ppm. An aqueous solution ($D_2O$) of disodium ethylene diphosphonate ($\delta 16.72$ ppm) is particularly useful as a secondary standard for aqueous samples because it gives no further correction for the type of the
spectrometer employed. There was a change in sign convention in the mid 1970s so that positive chemical shifts were downfield of the standard (this convention has again been reversed). Although modern NMR spectrometry can provide extremely accurate data when compounds are studied under a given set of conditions, this advantage is offset for many organophosphorus compounds by the dependence of their $^{31}$P NMR chemical shifts on concentration, solvent, and the presence of other compounds. $^{31}$P NMR spectroscopy can also provide a very convenient method for determining the optical purity of chiral phosphorus compounds. Thus when an enantiomer that forms an adduct with a phosphorus compound is added, different chemical shifts are often observed for the diastereomeric products.

The NMR chemical shifts of some phosphorus compounds are reported in Table 1 by class of compounds so that the relationships between chemical shifts and the substituent groups can be recognized. The $^1$H-decoupled NMR spectra were obtained on a Varian Model V-4300-2 high resolution spectrometer with a radio frequency of 16.2 Mc. and a magnetic field of approximately 9400 gauss, using a Varian magnet, Model V-4012-A. Chemical shifts are reported in parts per million (ppm) of the applied field using 85% H$_3$PO$_4$ as the external reference (zero shift). The data were obtained with pure samples of isolated compounds and identified independently by physical constants or elemental analysis. The solvents used are reported, since for some of the compounds, the chemical shifts depended somewhat on the solvents.
Table 1. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>δ (ppm)</th>
<th>Multiplicity</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₆H₅P)ₙ n = 2 or 4</td>
<td>Benzene</td>
<td>4.6</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₆H₅CH₂O)₂P(O)H</td>
<td>neat</td>
<td>-7.9</td>
<td>d</td>
<td>713</td>
</tr>
<tr>
<td>C₆H₅OP(O)Cl₂</td>
<td>neat</td>
<td>-1.8</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₆H₅O)₂P(O)Cl</td>
<td>neat</td>
<td>6.1</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₂H₅O)₂P(O)OH</td>
<td>aqueous</td>
<td>0</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>C₆H₅OP(O)(OH)₂</td>
<td>aqueous</td>
<td>4.8</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₆H₅O)₂P(O)OH</td>
<td>Methanol</td>
<td>12.7</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₆H₅CH₂O)₂P(O)OH</td>
<td>dioxane</td>
<td>1.1</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₂H₅)₂P(O)OP(O)(OC₂H₅)₂</td>
<td>neat</td>
<td>13.4</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₆H₅)₂P(O)OP(O)(OC₆H₅)₂</td>
<td>neat</td>
<td>23.9</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>(C₂H₅)₂Pₐ(OC₂H₅)OPₜ(O)-(OC₂H₅)OP(O)(OC₂H₅)₂</td>
<td>neat</td>
<td>+26.6(α)</td>
<td>d</td>
<td>16</td>
</tr>
<tr>
<td>(C₂H₅)₂P₇(OC₂H₅)OP(O)(OC₂H₅)₂</td>
<td>neat</td>
<td>+35.6 (β)</td>
<td>t</td>
<td>16</td>
</tr>
<tr>
<td>C₆H₅OP(O)NHC₆H₄NH₂</td>
<td>Ethanol</td>
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<td>t</td>
<td>15</td>
</tr>
<tr>
<td>(C₆H₅)₂P(O)NH₂</td>
<td>Methanol</td>
<td>-25.5</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

1.9.3 SPIN–SPIN COUPLING CONSTANTS

Since $^{31}$P is present in 100 % abundance and has a spin quantum number of $½$, $^{31}$P imparts spin-spin coupling information analogous to a proton coupling in $^{13}$C spectra. The multiplicity of phosphorus signals due to coupling to the neighboring protons is very useful for determining the nature and/or the number of aliphatic groups (including alkoxy and related groups) bound to the phosphorus atom. Phosphorus compounds exhibit a wide range of stereochemical changes that can be studied by recording the spectra of the samples at different temperatures. The spin-
spin coupling constants to phosphorous can also vary with temperature, usually due to altered rotational effects about the bond to phosphorus.58

1.9.4 BRUKER AC 300

FT NMR spectrometers fall into two main categories: those with water-cooled electromagnets operating with magnetic fields of 1.41–2.35 T, and those with superconducting solenoids cooled by liquid helium and operating with high magnetic fields of 3.5-9.39 T. When signal separation and sensitivity are the prime importance, such as in studies of biological systems, very high field spectrometers are necessary. Phosphorus compounds exhibit a wide range of stereochemical changes that can be studied by recording the spectra at different temperatures.58

1.9.5 17O AND 31P NMR STUDIES OF AROYLPHOSPHANES, AND AROYLPHOSPHONATES AND THE ABSENCE OF RESONANCE IN -COPR 2 GROUP

The 17O- and 31P NMR spectra for aryl-substituted p,p-diphenylbenzoyl-phosphanes and dialkylbenzoylphosphonates show a similar high subsistent sensitivity (P+), which explains a strong electron demand of the carbonyl group. Resonance stabilization was not possible with dialkyl benzoylphosphonates, which indicates that electron donation from phosphorus to carbonyl group is equally negligible. The 31P NMR shifts appears at low field and are less sensitive to the ring subsistent.61
1.9.6 $^{31}$P NMR STUDIES OF DIETHYL PHOSPHITE

$^{31}$P nuclear magnetic resonance spectroscopy has been used for distinguishing different types of chemical bonding in phosphorus compounds. It was used to determine the structure of intermediate species of sol derived from triethyl phosphate, calcium diethoxide, and acetic acid. NMR spectral data revealed that the reaction proceeds via a dialkyl phosphate intermediate. The proton coupled $^{31}$P experiment can reveal the magnitude of the spin-spin coupling between proton and phosphorus. The indirect spin-spin coupling between the alpha protons of the alkoxy substituents and phosphorus was easily detected by the coupling constant [$^3J(P-H)$] of about 7 Hz. Information about P-H bonds during the process was also determined from the splitting pattern and direct spin-spin constant [$^1J(P-H) ~ 600-800$ Hz]. The progress of a solution containing triethyl phosphite and calcium diethoxide in ethylene glycol and ethanol was monitored by $^{31}$P NMR for 24 hours, which showed a decrease in sharp peak intensity at 139 ppm and the appearance of a broad doublet at -100 ppm.$^{62}$
CHAPTER II

EXPERIMENTAL

2.1 INSTRUMENTATION AND MATERIALS :

$^1$H and $^{13}$C NMR spectra were obtained in CDCl$_3$ (Cambridge Isotopes) solution containing TMS (tetramethylsilane internal reference) on a Bruker AC300F NMR spectrometer. Chemical shifts were measured in parts per million relative to TMS as internal standard. Gold-level grade (507 HP) 5 mL NMR sample tubes were used in all experiments. $^{31}$P NMR spectra were obtained in different solvents (spectroscopic acetonitrile, ethyl acetate, deuterated chloroform CDCl$_3$ using 85% H$_3$PO$_4$ as internal standard).$^{63}$ GC/MS were obtained on a Varian 3900 GC using a Saturn 2100 T mass spectrometer with electron ionization.

Thermal analysis was obtained using a TA 2950 for TGA analysis and a TA 2920 for DSC analysis. Solvents and most of the reagents were purchased from Fisher Scientific Company or Aldrich Chemical Corporation. Chlorodiphenylphosphine (97%), dichlorophenylphosphine (98%), thionyl chloride, triethyl phosphite, toluoyl chloride, and pentafluorobenzoyl chloride were purchased from Aldrich Chemical Corporation and used as received. Petroleum ether was received
from Sigma Aldrich Chemical Corporation and was used as received. Benzene was received from Fisher Scientific and was purified by distillation over NaBH₄ under argon atmosphere. Carbon tetrachloride and cyclohexane were purchased from Aldrich Chemical Corporation and used as received. Benzoyl chloride was prepared by a literature procedure. N,N-Diethylaniline was purchased from sigma Aldrich and was dried with calcium hydride and distillation, other solvents were purified by simple distillation and were spectroscopic grade.

2.2 SYNTHESIS OF METHOXYDIPHENYLPHOSPHINE (I)

Preparation of compound I (methoxydiphenylphosphine) was adapted from a patent. To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer, dropping funnel, a water condenser with anhydrous calcium carbonate drying tube, and magnetic stirring assembly, an argon gas line was connected to supply a moisture-free environment. Then 13.5 mL of petroleum ether, 1.8 mL of N,N-diethylaniline and 1.7 mL of methanol were added together in the flask which was immersed in an ice bath at 0 °C. Then 2.25 mL of chlorodiphenylphosphine dissolved in 2.2 mL of petroleum ether was added drop wise over 20 minutes through an addition funnel to the previous mixture. The mixture was stirred for a further 2 hours in ice bath at 0º C temperature. After warming the mixture to about 5 ºC, the amine hydrochloride separated and was precipitated and removed by vacuum filtration, and the precipitate collected on the Hirsch funnel. To the filtrate 3 mL of cyclohexane were added and the mixture was first distilled at 10-20 mm Hg to remove all low boiling materials, then the solvents were removed from the distillate at reduced
pressure rotovapor, that process was repeated three times with the addition of 3 mL of
cyclohexane each time and rotovapor the excess methanol from the reaction media,
and a 1.96 g (88 %) of methoxydiphenylphosphine (I) ($^{31}$P NMR 115.75 ppm) as a
colorless oil was obtained.

2.3 SYNTHESIS OF BENZOYL DIPHENYLPHOSPHINE OXIDE (II) (1ST
ROUTE)

Compound II (benzoyldiphenylphosphine oxide) was adapted from a
patent, following the reaction scheme for the synthesis as explained in Figure
11. To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer,
dropping funnel, a water condenser with anhydrous calcium carbonate drying tube,
and magnetic stirring assembly, an argon gas line was connected to supply a
moisture-free environment. Then 2 mL of methoxydiphenylphosphine (I) previously
prepared dissolved in 2 mL of anhydrous toluene was added drop wise over 20
minutes to 1.6 mL of benzoyl chloride freshly prepared at room temperature 25º C
while stirring for two hour. After completion of the addition, the reaction was
allowed to continue for 30 minutes longer and then was cooled to 0-10º C. The color
of the reaction mixture changes from dark orange to pale yellow with white
precipitate, the product precipitated as a white powder and was collected by simple
vacuum filtration. The white precipitate was soluble in cyclohexane, and the solvents
were removed under reduced pressure. To the filtrate 2 mL of methylene chloride
and 2 mL of 10% sodium bicarbonate solution were added, two layers were formed
organic and aqueous. The organic layer was separated using separation funnel and the
excess solvent was removed under reduced pressure using rotovapor. To the residue 2 mL of cyclohexane was added and the solution was heated to 60-80°C in sand bath

\[
\text{Benzoic acid} + \text{Thionyl Chloride} \xrightarrow{80^\circ C} \text{Benzoyl Chloride}
\]

\[
\text{Chlorodiphenylphosphine} + \text{N,N-Diethylaniline} \xrightarrow{\text{Methanol}} \text{Methoxydiphenylphosphine}
\]

\[
\text{Methoxy diphenyl phosphate} + \text{Benzoyl Chloride} \xrightarrow{\text{Addition at 0.0 - 10 } ^\circ C / 20 \text{ min}} \Delta / 60 - 80 ^\circ C - 2.0 \text{ hrs} / \text{Argon} / \text{Toluene Anhydrous}
\]

\[
\text{Benzoyldiphenylphosphine Oxide}
\]

**Figure 11.** Synthesis of benzoyldiphenylphosphine oxide (II)
for 20 minutes, and then placed in ice bath for 5 minutes yellow crystals fell out of the solution, and the solvent was removed under reduced pressure. The yellow crystals were relatively insoluble in cyclohexane, but soluble in chloroform. The solvents were removed under reduced pressure to obtain 1.8 g (73%) yellow crystals of benzoyldiphenylphosphine oxide (II).

The UV-VS absorption spectrum of benzoyldiphenylphosphine oxide was determined in acetonitrile and methylene chloride. Solutions were prepared 25 mM with air as background, and a maximum was observed at 367 (580 M⁻¹ cm⁻¹). The literature value was 374 nm (563 M⁻¹ cm⁻¹). The melting point was determined to be 96-102º C (lit. 94-98 ºC).

2.4 SYNTHESIS OF BENZOYLDIPHENYLPHOSPHINE OXIDE (II) (2nd Route)

Compound II (benzoyldiphenylphosphine oxide) was also prepared according to the modified synthesis scheme from the literature and as adapted from a patent, following the reaction scheme for the synthesis as explained in Figure 12. Chlorodiphenylphosphine is reduced to the pyrophoric diphenylphosphine using lithium aluminum hydride under argon gas, followed by acylation with benzoyl chloride in the presence a tertiary amine (triethylamine). Oxidation to the acylphosphine oxide is accomplished using hydrogen peroxide.

Lithium aluminum hydride (20 mg, 1.98 mmol) was placed in Schlenk flask equipped with mechanical or magnetic stirrer, and a dropping funnel under argon atmosphere connected to a mineral oil gas bubbler. Anhydrous tetrahydrofuran
(THF, 8 mL) was added drop wise through dropping funnel and the mixture was stirred intensively in ice bath for 20 minutes. Chlorodiphenylphosphine (0.6 mL, 0.98 mmol) dissolved in 2 mL of anhydrous THF was added drop wise over 20 minutes by stirring continuously, occasional cooling with an ice bath was necessary because of the exothermic reaction. The reaction was stirred for two hours under argon gas flow, after completion of the reduction, the LiAlH₄ was filtered off under reduced pressure using fritted filter stick funnel with porosity A (coarse) using Celite-545 as filter agent, yielding diphenylphosphine (0.39g, 97%). CDCl₃ was added (1 mL) to 0.2 mL of the prepared diphenylphosphine and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

Acylation reaction was performed with benzoyl chloride (1.8 mL) dissolved in 5 mL of anhydrous toluene which was added to the reaction mixture right after the addition of triethylamine (1.4 mL, 1.2 mmol), and 1 g of K₂CO₃ to neutralize the generated HCl. The reaction was heated in sand bath at 50-60° C and stirred for two hours under argon. The amine salt was filtered off using a Hirsch funnel. After evaporation of the solvent under reduced pressure, the residue was diluted with anhydrous toluene (10 mL) and was oxidized by dropwise addition of a 30% hydrogen peroxide solution (0.5 mL, 1.24 mmol). After stirring for 20 minutes, the solution was diluted with ethyl acetate (20 mL) and extracted with a saturated NaHCO₃ solution (10 mL) and the organic layer was dried with Na₂SO₄. After evaporation of the solvent, the crude product was obtained as pale yellow precipitate (0.34 g) with 81% yield. CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.
Figure 12. New synthesis of benzoyle diphenylphosphine oxide (II).
2.5 SYNTHESIS OF DIBENZOYLPHENYLPHOSPHINE OXIDE (III)

Synthesis of compound III (dibenzoylphenylphosphine oxide) was adapted from a patent following the scheme in Figure 13 according to the Michaelis–Arbuzov reaction. Dichlorophenylphosphine was reduced to the pyrophoric phenylphosphine using LiAlH₄ under argon gas, followed by acylation with benzoyl chloride in the presence a tertiary amine (triethylamine). Oxidation to the acylphosphine oxide is accomplished using hydrogen peroxide.

Lithium aluminum hydride (60 mg, 2.98 mmol) was placed in Schlenk flask equipped with mechanical or magnetic stirrer, and a dropping funnel under argon atmosphere connected to a mineral oil gas bubbler. Anhydrous tetrahydrofuran (10 mL) was added drop wise through dropping funnel and the mixture was stirred intensively in ice bath for 20 minutes. Dichlorophenylphosphine (1 mL, 0.98 mmol) dissolved in 2 mL of anhydrous THF was added drop wise over 20 minutes by stirring continuously with occasional cooling with an ice bath. The reaction was stirred for two hours under argon. After completion of the reduction, excess LiAlH₄ was filtered off under reduced pressure using a fritted filter stick funnel with porosity A and Celite 545 as filter agent, yielding phenylphosphine 0.87 g (90%). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

The acylation was followed by addition of benzoic chloride (3.45 mL) in 5 mL of anhydrous toluene to the reaction mixture right after the addition of triethylamine (2.7 mL, 1.2 mmol) to neutralize the generated hydrochloric acid. The reaction was heated in silicon bath at 80-90°C and stirred for two hours under argon. The amine salt was filtered off using a Hirsch funnel. After evaporation of the
solvent under reduced pressure, the residue was diluted with anhydrous toluene (10 mL) and oxidized by dropwise addition of a 30% hydrogen peroxide solution (0.5 mL, 1.24 mmol). After stirring for 20 minutes, the solution was diluted with ethyl acetate (20 mL) and extracted with a saturated sodium bicarbonate solution (10 mL) and the organic layer was dried over sodium sulfate. After evaporation of the solvent, the crude product was obtained as bright yellow oil in (0.34g) 45% yield. CDCl₃ was added (1 mL) and the $^{31}$P, $^1$H, and $^{13}$C NMR spectra were recorded.

![Chemical Diagram](image)

**Figure 13.** Synthesis of dibenzoylphenylphosphine oxide (III).
2.6 SYNTHESIS OF TRIPHENYLPHOSPHINE OXIDE (IV)

Compound IV (triphenylphosphine oxide) was prepared by oxidation reaction of triphenylphosphine\textsuperscript{75} using benzoyl peroxide as an oxidizing agent in pentane following the synthesis scheme as explained in Figure 14.\textsuperscript{76,77}

To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer, dropping funnel, a water condenser with anhydrous calcium carbonate drying tube, and magnetic stirring assembly, and argon gas inlet, benzoyl peroxide (0.135 g, 1.125 mmol) was dissolved in 25 mL of warm pentane, and was added dropwise while

\[ \text{Triphenylphosphine} + \text{Benzoylperoxide} \rightarrow \text{Benzoic anhydried Triphenylphosphine oxide} \]

\textbf{Figure 14.} Synthesis of triphenylphosphine oxide (IV).
stirring to triphenylphosphine (0.145 g, 1.125 mmol) in 7.5 mL of warm pentane. The reaction was stirred under argon for one hour, and triphenylphosphine oxide was obtained by evaporation of excess solvent under reduced pressure and filtration through Hirsch funnel.77

2.7 SYNTHESIS OF (2,4,6-TRIMETHYLBENZOYL)DIPHENYL-PHOSPHINE OXIDE (V)

Compound V [(2,4,6-trimethylbenzoyl)diphenylphosphine oxide] was adapted from a patent,71 following the reaction scheme in Figure 16 according to the Michaelis-Arbuzov reaction.73,74 Chlorophenylphosphine is reduced to the pyrophoric phenylphosphine using lithium aluminum hydride under argon, followed by acylation with freshly prepared 2,4,6-trimethylbenzoyl chloride in the presence a tertiary amine (triethylamine). Oxidation to the acylphosphine oxide is accomplished using benzoyl peroxide.

2.7.1 PREPARATION OF 2,4,6-TRIMETHYLBENZOYL CHLORIDE

2,4,6-Trimethylbenzoyl chloride was prepared according to the literature64 as shown in Figure 15. To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer, dropping funnel, a water condenser with anhydrous calcium carbonate drying tube, and magnetic stirring assembly, an argon line was connected and 3 mL of 2,4,6-trimethylbenzoic acid dissolved in 25 mL of anhydrous warm benzene was added dropwise while stirring to 4 mL of thionyl chloride. The reaction was stirred for two hours after the addition of K₂CO₃ to neutralize the HCl evolved. The
potassium carbonate was filtered off using Celite-545, and the 2,4,6-trimethylbenzoyl chloride was refluxed for two hours at 80º C under argon. The excess thionyl chloride and benzene were removed by simple distillation. After completion of the distillation, the reaction was heated for an additional half hour, and the residue was 2,4,6-trimethylbenzoyl chloride (2.65 mL, 88%) with boiling point of 148° C. CDCl₃ was added (1 mL) and the ¹H, and ¹³C NMR spectra were recorded.

![Figure 15. Preparation of 2,4,6-trimethylbenzoyl chloride](image)

2.7.2 SYNTHESIS OF 2,4,6-TRIMETHYLBENZOYLDPHENYL PHOSPHINE OXIDE (V)

Synthesis of compound V [(2,4,6-trimethylbenzoyl)phenylphosphine oxide] was adapted from a patent, following the synthesis in Figure 16. According to Michaelis-Arbuzov reaction, lithium aluminum hydride (60 mg, 2.98 mmol) was placed in Schlenk flask equipped with magnetic stirrer and dropping funnel under argon atmosphere connected to a mineral oil gas bubbler. Anhydrous tetrahydrofuran (10 mL) was added dropwise through a dropping funnel, and the mixture was stirred vigorously in an ice bath for 20 minutes. Chlorodiphenylphosphine (1 mL, 0.98 mmol) dissolved in 2 mL of anhydrous THF was added drop wise over 20 minutes by
stirring continuously with occasional cooling in an ice bath. The reaction was stirred for two hours under argon, after which excess LiAlH₄ was filtered off under reduced pressure using fritted filter stick funnel with porosity A and Celite-545 as filter agent, yielding 0.81 mL of diphenylphosphine (85%). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

The acylation reaction was followed by addition of 2,4,6-trimethylbenzoyl chloride (3.0 mL) dissolved in 5 mL of anhydrous benzene following addition of triethylamine (2.7 mL, 1.2 mmol) added to neutralize the generated hydrochloric acid. The reaction was heated in silicon oil bath at 80-90° C and stirred for two hours under argon. The amine salt was filtered off using a Hirsch funnel. After evaporation of the solvent under reduced pressure, the residue was diluted with anhydrous toluene (10 mL) and was oxidized by drop wise addition of a 30% hydrogen peroxide solution (0.5 mL, 1.24 mmol). After stirring for 20 minutes, the solution was diluted with ethyl acetate (20 mL), extracted with a saturated sodium bicarbonate solution (10 mL), and the organic layer was dried with sodium sulphate after evaporation of the solvent. The crude product was obtained as bright yellow crystals 0.53 g (45% yield). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.
Figure 16. Synthesis of (2,4,6-trimethylbenzoyl)phenylphosphine oxide (V)
2.8 ATTEMPTED SYNTHESIS OF \textit{bis}(2,4,6-TRIMETHYLBENZOYL)-PHENYLPHOSPHINE OXIDE (VI)

Synthesis of compound VI [\textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine oxide] was adapted from a patent\textsuperscript{65} following the reaction scheme in Figure 17 according to Michaelis–Arbuzov reaction\textsuperscript{66,67}. Dichlorophenylphosphine is reduced to the pyrophoric phenylphosphine using lithium aluminum hydride in a 1:2 molar ratio under argon, as indicated in Figure 13, followed by acylation with freshly distilled 2,4,6-trimethylbenzoyl chloride (2.2 eq) in the presence of pyridine. \textit{bis}(2,4,6-Trimethylbenzoyl)phenylphosphine was obtained, and the mechanism of the acylation in the presence of pyridine was explained in the result and discussion section. CDCl\textsubscript{3} was added (1 mL) and the \textsuperscript{31}P, \textsuperscript{1}H, and \textsuperscript{13}C NMR spectra were recorded. Attempted oxidation of the \textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine to \textit{bis}(2,4,6-trimethylbenzoyl)phenylphosphine oxide using benzoyl peroxide failed, affording a mixture of unidentified materials.

2.9 SYNTHESIS OF METHOXYPHENYLPHOSPHINE OXIDE (VII)

Compound VII (methoxyphenylphosphine oxide) was prepared following the modified synthesis literature\textsuperscript{79} and the reaction scheme as shown in Figure 18. To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer, dropping funnel, a water condenser with anhydrous calcium carbonate drying tube, and magnetic stirring assembly, an argon gas line was connected to supply a moisture-free environment. Then 8.5 mL of petroleum ether, 2 mL of \textit{N,N-diethylaniline}, and 4 mL
of methanol were added together in the flask which was immersed in an ice bath at 0ºC, then 1.25 mL of dichlorophenylphosphine dissolved in 2.5 mL of petroleum ether

\[
\text{Ph-P-Cl} \xrightarrow{\text{Reduction/ LiAlH}_4} \text{Ph-P-H} + 2\text{HCL}
\]

Dichlorophenylphosphine

\[
\text{CH}_3 \text{C} = \text{O} - 2\text{HCL}
\]

2,4,6-trimethylbenzoylchloride

\[
\text{Ph} \quad \text{P} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{Ph}
\]

Acylation / pyridine

\[
\text{CH}_3
\]

Oxidation

\[
\text{Ph} \quad \text{P} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{Ph}
\]

Bis(2,4,6-trimethylbenzoyl)phenyl phosphine

\[
\text{CH}_3
\]

Bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide

**Figure 17.** Synthesis of bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (VI).
was added drop wise over 20 minutes through an addition funnel to the previous mixture. The mixture was stirred for a further 2 hours in ice bath to maintain 0º C temperature was placed in the dark hood. After completion of the reaction, it was warmed to about 5 ºC, the amine hydrochloride separated and was precipitated and removed by vacuum filtration, and the precipitate collected on a Hirsch funnel.

To the filtrate, 2 mL of cyclohexane were added and the mixture was first distilled under vacuum at 10-20 mm Hg to remove all low boiling materials. The solvents were removed from the distillate at reduced pressure, and that process was repeated three times with the addition of 2 mL of cyclohexane each time to remove residual methanol. Methoxyphenylphosphine oxide (VI) was obtained as 0.96 g (75%) yellow oil. CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded. ³¹P NMR: d, pentet 25.43 ppm (lit.⁶³ -25.2 ppm due to opposite sign convention).

![Diagram of synthesis](image)

**Figure 18.** Synthesis of methoxyphenylphosphine oxide (VII).
2.10 ATTEMPTED SYNTHESIS OF DIMETHOXYPHENYLPHOSPHINE (VIII)

Compound VIII (dimethoxyphenylphosphine) was prepared following a modified synthesis from the literature\textsuperscript{80} according to the reaction scheme as shown in Figure 20. To a dry 100 mL 3-neck round-bottom flask equipped with a thermometer, dropping funnel, a water condenser with anhydrous calcium carbonate drying tube, and magnetic stirring assembly, an argon line was connected to supply a moisture-free environment. Reaction of dichlorophenylphosphine (1.0 mL, 1 mol) with 2 equivalents of methanol in petroleum ether (4.0 mL) as solvent, in the presence of 2 mL of \textit{N,N-diethylaniline} following the method of Abuzov and Razumov.\textsuperscript{81} The amine hydrochloride separated and was precipitated and removed by vacuum filtration, and the precipitate collected on a Hirsch funnel. The excess methanol was removed under reduced pressure, and the dimethoxyphenylphosphine was obtained as pale yellow solution with boiling point of 198-205° C in 24% yield and was unsuccessfully purified. CDCl\textsubscript{3} was added (1 mL) and the \textsuperscript{31}P, \textsuperscript{1}H, and \textsuperscript{13}C NMR spectra were recorded.

\begin{center}
\begin{tikzpicture}
  \node (a) at (0,0) {\text{Dichlorophenylphosphine}};
  \node (b) at (4,0) {\text{Dimethoxyphenyl phosphine}};
  \node (c) at (2,1) {\text{2 CH\textsubscript{3}OH / Petroleum Ether}};
  \node (d) at (2,0) {\text{\textit{N,N Diethylaniline}}};
  \draw[->] (a) -- (c) node[midway,above] {Cl};
  \draw[->] (c) -- (b) node[midway,above] {OCH\textsubscript{3}};
  \draw[->] (c) -- (b) node[midway,below] {OCH\textsubscript{3}};
  \draw[->] (c) -- (b) node[midway,above] {+ 2 HCl};
\end{tikzpicture}
\end{center}

\textbf{Figure 19.} Synthesis of dimethoxyphenylphosphine (VIII).
2.11 SYNTHESIS OF \( P\)-TOLUOYLDIPHENYLPHOSPHINE OXIDE(IX)

2.11.1 SYNTHESIS OF \( P\)-TOLUOYLDIPHENYLPHOSPHINE OXIDE (IX) (1st Route)

Synthesis of compound VIII (\( p\)-toluoyldiphenylphosphine oxide) was adapted from a patent, following the reaction scheme for the synthesis in Figure 20 according to the Michaelis–Arbuzov reaction. Lithium aluminum hydride (60 mg, 1.0 mmol) was placed in Schlenk flask equipped with mechanical or magnetic stirrer, and a dropping funnel under argon atmosphere connected to a mineral oil gas bubbler. Anhydrous THF (10 mL) was added drop wise through dropping funnel and the mixture was stirred intensively in ice bath for 20 minutes. Chlorodiphenylphosphine (1 mL, 0.98 mmol) dissolved in 2 mL of anhydrous THF was added dropwise over 20 minutes with stirring continuously and occasional cooling with an ice bath. The reaction was stirred for two hours under argon, and after completion of the reduction the LiAlH\(_4\) was filtered off under reduced pressure using fritted filter stick funnel with porosity A (coarse) with Celite-545 as filter agent, yielding diphenylphosphine 0.87g (84.5%). CDCl\(_3\) was added (1 mL) and the \( ^{31}\)P, \(^1\)H, and \(^{13}\)C NMR spectra were recorded.

The acylation reaction was performed with toluoyl chloride (1.125 mL) dissolved in 5 mL of anhydrous toluene added to the reaction mixture right after the addition of triethylamine (1.4 mL, 1.2 mmol) and 1 g of \( K_2CO_3\). The reaction was stirred at 110° C in a silicon oil bath for two hours under argon. The amine salt was filtered off through a Hirsch funnel. After evaporation of the solvent under reduced pressure, the residue was diluted with anhydrous toluene (10 mL) and was oxidized
by dropwise addition of a benzoyl peroxide solution (1.0 g, 1.24 mmol). After stirring for 60 minutes, the solution was diluted with ethyl acetate (20 mL), extracted with a saturated NaHCO₃ solution (10 mL), and the organic layer was dried with Na₂SO₄. After evaporation of the solvent, the crude product was obtained as sharp needle crystals 0.61g (72 % yield). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

**Figure 20.** Synthesis of p-toluoyldiphenylphosphine oxide (IX) (1st Route)
2.11.2 SYNTHESIS OF P-TOLUOYLDIPHENYLPHOSPHINE OXIDE (IX) (2nd Route)

Synthesis of compound IX (p-toluoyldiphenylphosphine oxide) was adapted from a patent, following the reaction scheme in Figure 21. In a flask equipped with magnetic stirrer, dropping funnel under argon atmosphere connected to a mineral oil gas bubbler, 2 mL of methoxydiphenylphosphine (I) previously prepared as explained in Figure 11, was dissolved in 2 mL of anhydrous toluene and added dropwise over 20 minutes to 1.6 mL of toluoyl chloride freshly prepared at 25°C with stirring for two hour. After completion of the addition, the reaction was heated in an oil bath to 80–90°C for 60 minutes and then was cooled to 0-10°C. The color of the reaction mixture changes from bright to pale yellow with a white precipitate; the product precipitated as a white powder and was collected by simple vacuum filtration. The precipitate was purified by dissolving in cyclohexane, and left in the refrigerator.

![Chemical reaction diagram](image)

**Figure 21.** Synthesis of p-toluoyldiphenylphosphine oxide (IX) (2nd Route)
overnight to grow 1.8 g (60%) of colorless crystals of \( p \)-toluoyldiphenylphosphine oxide (VIII). The crystals were relatively insoluble in cyclohexane, but soluble in chloroform, so CDCl\(_3\) was added (1 mL) and the \( ^{31}\)P, \( ^1\)H, and \( ^{13}\)C NMR spectra recorded.

### 2.12 SYNTHESIS OF 2,6-DIMETHOXYBENZOYLDIPHENYL PHOSPHINE OXIDE (X)

Compound (X) [(2,6-dimethoxybenzoyl)diphenylphosphine oxide] was prepared following the scheme in Figure 22, according to the Michaelis–Arbuzov reaction.\(^{65,66,71}\) Methoxydiphenylphosphine I (1 mL) previously prepared as explained in Figure 11, and was dissolved in 2 mL of anhydrous toluene was added drop wise over 20 minutes to 2 mL of 2,6-dimethoxybenzoyl chloride at room temperature 25ºC while stirring for two hour. After completion of the addition, the reaction was heated in an oil bath to 90ºC and allowed to continue for 2 hours and then was cooled to 0-10ºC. The color of the reaction mixture changes from colorless to yellow. The product was purified by dissolving the reaction mixture in cyclohexane, and let it cool dawn in the refrigerator overnight to grow the crystals which fall of the solution, the excess solvents were removed under reduced pressure. The crystals were relatively insoluble in cyclohexane, but soluble in chloroform. The solvents were removed under reduced pressure to obtain 1.2 g (85%) colorless needle crystals of 2,6-dimethoxybenzoyl oxide (IX). CDCl\(_3\) was added (1 mL) and the \( ^{31}\)P, \( ^1\)H, and \( ^{13}\)C NMR spectra were recorded.
2.13 SYNTHESIS OF (PENTAFLUOROBENZOYL)DIPHENYLPHOSPHINE OXIDE (XI)

2.13.1 PREPARATION OF PENTAFLUOROBENZOYL CHLORIDE

Pentafluorobenzoyl chloride was prepared according to the literature procedure following the reaction scheme in Figure 23. In a round-bottom flask equipped with a magnetic stirrer, a dropping funnel under argon atmosphere connected to a mineral oil gas bubbler, pentafluorobenzoic acid (2.0 g) dissolved in 10 mL of anhydrous benzene freshly distilled, was added dropwise while stirring over 20 minutes to thionyl chloride (6.0 mL) and the mixture was refluxed for 16 hours. The excess thionyl chloride was removed under reduced pressure, and the residue was distilled under vacuum. The pentafluorobenzoyl chloride was collected as a slightly yellow oil after evaporation of the excess solvent under reduced pressure, yield 1.78 g (80%), boiling point 178-186°C.
Figure 23. Synthesis of 2,3,4,5,6-pentafluorobenzoyl chloride

2.13.2 SYNTHESIS OF (PENTAFLUOROBENZOYL)DIPHENYL-PHOSPHINE OXIDE (XI)

Synthesis of compound XI [(pentafluorobenzoyl)diphenylphosphine oxide] was adapted from a patent\textsuperscript{84} and was prepared following the modified reaction shown in Figure 24, according to Michaelis–Arbuzov reaction\textsuperscript{66,71}. Lithium aluminum hydride (60 mg, 1.0 mmol) was placed in Schlenk flask equipped with mechanical or magnetic stirrer, and a dropping funnel under argon atmosphere connected to a mineral oil bubbler. Anhydrous tetrahydrofuran (10 mL) was added dropwise through a dropping funnel and the mixture was stirred intensively in ice bath for 20 minutes. Chlorodiphenylphosphine (1 mL, 0.98 mmol) dissolved in 2 mL of anhydrous THF was added drop wise over 20 minutes by stirring continuously, occasionally cooling with an ice bath. The reaction was stirred for two hours under argon. After completion of the reduction, the excess LiAlH\textsubscript{4} was filtered off under reduced pressure using a fritted filter stick funnel with porosity A and Celite-545 as filter agent, yielding 0.92 mL of diphenylphosphine (95%). CDCl\textsubscript{3} was added (1 mL) and the $^{31}$P, $^1$H, and $^{13}$C NMR spectra were recorded.
The acylation reaction was initiated using freshly prepared 2,3,4,5,6-pentafluorobenzoyl chloride (0.85 mL) dissolved in 5 mL of anhydrous toluene together with K₂CO₃ (1.0 g) which was added to the reaction mixture to neutralize the generated hydrochloric acid. The reaction was stirred at 110°C in a mineral oil bath for two hours under argon. The insoluble salts were filtered off through a Hirsch funnel. After evaporation of the solvent under reduced pressure, the ³¹P, ¹H, and ¹³C NMR spectra of (pentafluorobenzoyl)diphenylphosphine were recorded. The residue was diluted with anhydrous toluene (10 mL) and oxidized by dropwise addition of a benzoyl peroxide solution (1.0 g, 1.24 mmol in 2 mL of toluene). The reaction was stirred for 60 minutes, and the excess solvent was removed under reduced pressure. The crude product was obtained as bright yellow residue, 0.53 g (62%). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

2.14 ATTEMPTED SYNTHESIS OF (3,5-DINITROBENZOYL)DIPHENYL-PHOSPHINE OXIDE (XII)

Synthesis of compound XII [(3,5-dinitrobenzoyl)diphenylphosphine oxide] was adapted from a patent, following the reaction scheme in Figure 25 according to the Michaelis-Arbuzov reaction. Lithium aluminum hydride (60 mg, 1.0 mmol) was placed in a Schlenk flask equipped with magnetic stirrer and a dropping funnel under argon atmosphere connected to a mineral oil gas bubbler. Anhydrous THF (10 mL) was added dropwise through a dropping funnel and the mixture with vigorous stirring in an ice bath for 20 minutes. Chlorodiphenylphosphine (0.6 mL,
Figure 24. Synthesis of (2,3,4,5,6-pentafluorobenzoyl)diphenylphosphine oxide (XI)

0.98 mmol) dissolved in 2 mL of anhydrous THF was added dropwise over 20 minutes by stirring continuously with occasional cooling in an ice bath. The reaction was stirred for two hours under argon. After completion of the reduction, the excess
LiAlH₄ was filtered off under reduced pressure using fritted filter stick funnel (porosity A) using Celite-545 as filter agent, yielding diphenylphosphine in 0.91 ml 90% yield. CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

The acylation reaction was preceded by dissolving freshly distilled 3,5-dinitrobenzoyl chloride (1.25 gm) in anhydrous benzene, which was determined by NMR to be a mixture of the acid, anhydride, and acid chloride. Therefore, 1.0 mL of thionyl chloride was added to convert the mixture to the acid chloride.

The acylation reaction proceeded by the addition of excess (1.4 eq) acid chloride in 5 mL of anhydrous benzene after the addition of triethylamine (1.4 mL, 1.2 mmol), and 1g K₂CO₃ which was added to the reaction mixture to neutralize the generated hydrochloric acid. The color of the reaction changes from clear to reddish brown and was stirred at room temperature for two hours under argon. The amine salt was filtered off through a Hirsch funnel. After evaporation of the solvent under reduced pressure using vacuum pump using a liquid nitrogen trap for 24 hours, the residue was dissolved in 10 mL of cyclohexane and was refluxed for two hours, then cooled to room temperature. The (3,5-dinitrobenzoyl)diphenylphosphine was obtained as yellow crystals (65% yield). CDCl₃ was added (1 mL) and the ³¹P, ¹H, and ¹³C NMR spectra were recorded.

Oxidation was attempted using 2.0 g of benzoyl peroxide, and the (3,5-dinitrobenzoyl)diphenylphosphine oxide which was obtained unsuccessfully purified due to the dimerization of the product as was characterized by ³¹P NMR (see results section).
Figure 25. Synthesis of (3,5-dinitrobenzoyl)diphenylphosphine oxide (XII)
2.15 IRRADIATION OF MODEL COMPOUNDS OF MONO- AND DI-MESITOYLPHOSPHINE OXIDE

Solutions of 1 mM (trimethylbenzoyl)diphenylphosphine oxide (commercially available as TPO) and bis(trimethylbenzoyl)phenylphosphine oxide (commercially available as Irgacur 819) were prepared from pure compounds used as received from Ciba Chemicals and Sigma Aldrich. These compounds were soluble in ethyl acetate, acetonitrile, chloroform, dichloromethane, benzene, and ethanol. All irradiations were carried out in Pyrex vessels equipped with a magnetic stir bar and a reflux condenser. Four unfiltered 350-nm 250 W sun lamps placed about 10 inches away were used as the light source. The solutions were flushed with argon before and during the irradiation. Aliquots were removed intervals of 30, 60, 120 and 240 minutes, and the solvents were evaporated under reduced pressure (50 ºC at 20 mbar). The residue was dissolved in 2 mL of CDCl₃ and the ³¹P, ¹H, and ¹³C NMR spectra were recorded. For example, Irgacur -819 bis(trimethylbenzoyl)phenylphosphine oxides showed a pentet at δ = 4.84 ppm before irradiation, and after irradiation three different phosphorus-containing compounds were observed in Figure 133 at δ = 15.6, 17.8 and 19.5 ppm in a ratio of 1:2:8, respectively.

2.16 POLYMERIZATION OF METHYL METHACRYLATE AND ACRYL AMIDE WITH SELECTED MONO- AND DI-ACYLPHOSPHINE OXIDES BY DSC

The thermal stability of mono- and di-acylphosphine oxides was examined by differential scanning calorimetry (DSC). Endothermic and exothermic reactions of
the two initiators were observed. The DSC operating program was: 10°C/min.,
nitrogen atmosphere, flow rate 80 mL/min., in an aluminum pan with crimped lid,
temperature range from 25 to 300°C, and a sample size of 20-25 mg. The DSC was
calibrated with indium melting at 157°C with a heat of fusion of 28.4 J/g.
The thermal analysis study examines the polymerization in a DSC cell, of dental
monomers catalyzed by synthesized acylphosphine oxides. This part of the research
focuses on establishing a relationship between the free radicals generated by the
initiator, and their kinetic reaction rates with the monomer, methyl methacrylates and
acryl amide were used as model monomer. Benzoyl peroxide was employed to
evaluate the DSC response to exothermic polymerization heats and rates and compare
the results with the literature. The research indicates that the mono- and di-
acylphosphine oxides were differentiated by the relative reaction rate (W/g/min) but
not the overall heat of polymerization, $\Delta H_{pzn} (J/g)$. Auto-polymerization of acryl
amide and decomposition of benzoyl peroxide to form free radicals was also
measured. The combination of acryl amide/benzoyl peroxide (90/10 wt) enhanced the
relative reaction rate significantly. The acryl amide model system laid the ground
work for the critical evaluation of the synthesized (2,4,6-trimethylbenzoyl)diphenyl-
phosphine oxide and bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide. The
diacylphosphine oxide initiator was more reactive than the monoacylphosphine oxide
initiator with methylmethacrylates under laboratory conciliations. The exothermic
polymeric reaction in the lab reactor produced temperatures that rose higher and more
rapidly for the diacylphosphine oxide catalyst. Thermal and kinetic polymerization
properties of the new synthetic acylphosphine oxides were measured in the liquid
state by DSC. The measurements used were polymerization heat (W/g) and rate (mW/g/min) as a function of temperature (°C) and time (min). Each monomer, acrylamide (ACM), methyl methacrylates (MMA), and catalyst also were examined by DSC to determine their melting, decomposition, and thermal polymerization properties.
CHAPTER III
SPECTROSCOPIC CHARACTERIZATIONS

In the course of our studies of the synthesis of the series of monoacylphosphine oxide and diacylphosphine oxide photoinitiators, chlorodiphenylphosphine and dichlorophenylphosphine were chosen as the starting material for the synthesis of all mono- and di-acylphosphine oxides, respectively. The spectroscopic properties of the chlorophenylphosphines were investigated and were consistent with those expected for these starting materials. The proton-coupled $^{31}$P NMR (121.5 Hz) spectrum of chlorodiphenylphosphine showed a resonance at $\delta = 82.6$ ppm (triplet, $J = 9$ Hz), which is a singlet in the spectrum.

The proton-coupled $^{31}$P NMR (121.5 MHz) of dichlorophenylphosphine showed a resonance at $\delta = 161.06$ ppm (pentet, $J = 18$ Hz) which also is a singlet in the proton-decoupled spectrum ($\delta = 161.0$ ppm).

3.1 BENZOYLDIPHENYLPHOSPHINE OXIDE (II)
3.1.1 METHOXYDIPHENYLPHOSPHINE (I)

\[
\begin{align*}
\text{P} & \quad \text{OCH}_3 \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\(^{31}\text{P}\) NMR (121 MHz, CDCl\(_3\)): \(\delta = 115.75\) ppm (octet, \(J = 8.0\) Hz); \(^{13}\text{C}\) NMR (50 MHz, CDCl\(_3\)): \(\delta = 26.86, 56.46, 56.83, 77.00, 128.20, 128.34, 128.69, 129.29, 130.10, 130.53, 141.28, 141.65\); \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 3.74\) (d, 8.0 Hz), 7.41, 7.43, 7.58.

3.1.2 BENZOYLDIPHENYLPHOSPHINE

\[
\begin{align*}
\text{P} & \quad \text{O} \\
\text{Ph} & \quad \text{C} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\(^{31}\text{P}\) NMR (121 MHz, CDCl\(_3\)): \(\delta = 11.2\) ppm; \(^{13}\text{C}\) NMR (50 MHz, CDCl\(_3\)): \(\delta = 127.86, 128.14, 128.46, 129.29, 129.48, 130.08, 130.92, 131.38, 132.13, 133.83, 134.08, 134.89, 161.9\) and the carbonyl group C=O (196.36, d, 43 Hz); \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.23, 7.24, 7.54, 7.63, 7.89, 8.01.\)
3.1.3 BENZOYLDIPHENYLPHOSPHINE OXIDE (II)

\[
\begin{align*}
\text{P} & \quad \text{O} \\
\text{O} & \quad \text{C} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

\[\text{\ce{31P NMR (121 MHz, CDCl3): } \delta = 21.79 \text{ ppm (pentet, 11.2 Hz); } \text{\ce{13C NMR (50 MHz, CDCl3): } \delta = 128.39, 129.29, 131.46, 132.81, 135.84, 137.21, 140.16, \text{ and } 195.87 \text{ (carbonyl, d, } J = 46 \text{ Hz); } \text{\ce{1H NMR (300 MHz, CDCl3): } \delta = 7.40, 7.60, 8.21, \text{ and } 8.63.}\}
\]

3.1.4 CHLORODIPHENYLPHOSPHINE

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{P} & \quad \text{Cl}
\end{align*}
\]

\[\text{\ce{31P NMR (121.5 Hz) } \delta = 82.6 \text{ ppm (t, 9 Hz); } \text{\ce{13C NMR (50 MHz, CDCl3): } 131.34 \text{ (o, d, 30.21 Hz), } 129.06 \text{ (m, d, 7.58 Hz), } 141.33 \text{ (i, d, 52.85 Hz).}\}
\]
3.1.5 DIPHENYLPHOSPHINE

![Structure of Diphosphine](image)

$^{31}$P NMR (121 MHz, CDCl$_3$): $\delta = -42.6$ ppm (dt, 102 and 7 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 127.98, 128.03, 128.15, 129.6, 131.46, 133.32$; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 4.36$ (d, 102 Hz), 5.63, 4.18, 7.26, 7.34, 7.54.

3.1.6 UV-VIS SPECTRAL ANALYSIS OF BENZOYLDIPHENYLPHOSPHINE OXIDE (II)

The UV-VIS absorption spectrum of benzoyldiphenylphosphine oxide was determined in acetonitrile and methylene chloride. Solutions were prepared of 25 mM with air as background, a maximum was observed at wavelength of 367 nm and extinction coefficient of 580 M$^{-1}$ cm$^{-1}$ (Figure 26). The literature maximum wavelength was reported at 374 nm with extinction coefficient 563 M$^{-1}$ cm$^{-1}$. The melting point was determined to be 96-102° C (literature 94-98° C).
Figure 26. UV-VIS absorption spectra of benzoyldiphenylphosphine oxide at 25° C

3.2 DIBENZOYLPHENYLPHOSPHINE OXIDE (III)

3.2.1 DICHLOROPHENYLPHOSPHINE

![Chemical structure of dichlorophenylphosphine]

$^{31}$P NMR (121 MHz, CDCl$_3$): $\delta = 161.06$ ppm; $^{13}$C NMR (50 MHz, CDCl$_3$):

130.04, ($o$, d, 31.23 Hz), 128.86, ($m$, d, 7.88 Hz), 140.33, ($i$, d, 51.85 Hz).
3.2.2 PHENYLPHOSPHINE

\[ \text{\[
\begin{array}{c}
\text{H} \\
\text{P} \\
\text{H}
\end{array}
\]}
\]

\(^{31}\)P NMR (121 MHz, CDCl\textsubscript{3}): \(\delta = -124.53\) (tt, 199.84 and 7.0 Hz); \(^{13}\)C NMR (50 MHz, CDCl\textsubscript{3}): \(\delta = 13.99, 22.56, 25.54, 31.50, 67.88, 77.00, 127.6\) (\(p\)), \(127.99\) (\(m, d\)), \(127.96\) (\(ipso\)), \(134.25\) (\(o, d\)). The literature\textsuperscript{86} values were reported, \(^{31}\)P NMR (THF): \(\delta = -125.7\) (tt, 198.7 and 6.9 Hz); \(^{13}\)C NMR (THF): \(128.8\) (\(p\)), \(129.19\) (\(m, d, 5.9\) Hz), \(129.16\) (\(i, 8.8\) Hz), \(135.45\) (\(o, d, 16.2\) Hz); \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 4.10\) (\(d, 201\) Hz), 7.26, 7.38, 7.59.

3.2.3 DIBENZOYLPHENYLPHOSPHINE

\[ \text{\[
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{P} \\
\text{C} \\
\text{O} \\
\end{array}
\]}
\]

\(^{31}\)P NMR (121 MHz, CDCl\textsubscript{3}): \(\delta = 28.82\) ppm; \(^{13}\)C NMR (50 MHz, CDCl\textsubscript{3}): \(\delta = 8.77, 21.31, 46.58, 77.00, 125.18, 128.10, 128.9, 131.26, 135.24, 137.69,\) carbonyl 195.33 (\(d, 47\) Hz); \(^1\)H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 7.23, 7.24, 7.54, 7.89, 8.01.\)
3.2.4 DIBENZOYLPHENYLPHOSPHINE OXIDE (III)

\[
\begin{align*}
\text{O} & \quad \text{C} & \quad \text{O} \\
\text{C} & \quad \text{P} & \quad \text{C} \\
\text{C} & \quad \text{H} & \quad \text{C} \\
\end{align*}
\]

\(^{31}\text{P}\) NMR (121 MHz, CDCl\(_3\)): \(\delta = 18.26\) ppm; \(^{13}\text{C}\) NMR (50 MHz, CDCl\(_3\)): \(\delta = 21.20, 77.00, 126.67, 128.37, 128.59, 128.96, 132.08, 132.25, 132.83, 132.89, 135.23, 135.49, 136.07, 140.04\), carbonyl 192.17 (d, 46 Hz); \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.28, 7.31, 7.36, 7.38, 7.40, 7.45, 8.20\).

3.2.5 UV-VIS SPECTRAL ANALYSIS OF BENZOYLDIPHENYL PHOSPHINE OXIDE (II) AND DIBENZOYLPHENYLPHOSPHINE OXIDE (III)

The UV-VIS absorption spectra of dibenzoylphenylphosphine oxide and benzoyldiphenylphosphine oxide were determined in acetonitrile. Solutions were prepared 10 mM with air as background. Maxima were observed for dibenzoylphenylphosphine oxide at wavelengths of 367 and 380 nm with extinction coefficients 80.8 and 100.1 M\(^{-1}\) cm\(^{-1}\) respectively, as well as two shoulders at 352 and 395 nm with extinction coefficients of 15.9 and 74.0 M\(^{-1}\) cm\(^{-1}\) respectively (Figure 27). A maximum was observed for benzoyldiphenylphosphine oxide for the same concentration at 367 nm with extinction coefficient of 14.5 M\(^{-1}\) cm\(^{-1}\).
Figure 27. UV-VIS absorption spectra of benzoyldiphenylphosphine oxide(II) and dibenzoylphenylphosphine oxide in acetonitrile at 25°C

3.3 TRIPHENYLPHOSPHINE OXIDE (IV)

\[
\begin{align*}
\text{PHO(COPh)}_2 & \quad \text{PHO(COPh)}
\end{align*}
\]

\[^{31}\text{P NMR (121 MHz, CDCl}_3\text{): } \delta = 27.36 \text{ ppm (octet); } ^{13}\text{C NMR (50 MHz, CDCl}_3\text{): } \delta = 77.00, 128.31, 128.55, 131.48, 131.83, 131.89, 131.93, 132.12, 133.55; \]

\[^{1}\text{H NMR (300 MHz, CDCl}_3\text{): } \delta = 7.49, 7.53, 7.56, 7.65, 7.69, 7.71.\]
3.4 (2,4,6-TRIMETHYLBENZOYL)DIPHENYLPHOSPHINE OXIDE (V)

3.4.1 2,4,6-TRIMETHYLBENZOIC ACID

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{OH} \\
\text{CH}_3 & \quad \text{C} \\
\text{CH}_3 & \quad \text{H}_3
\end{align*}
\]

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 21.13$ (p-methyl), 20.30 (o-methyl), 128.78 (benzene solvent), 129.0 (o), 128.6 (m), 136.14 (i), 140.06 (para), 175.216 (carboxyl).

3.4.2 2,4,6-TRIMETHYLBENZOYL CHLORIDE

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{CH}_3 & \quad \text{Cl} \\
\text{CH}_3 & \quad \text{C} \\
\text{CH}_3 & \quad \text{H}_3
\end{align*}
\]

$^{13}$C NMR (50 MHz, CDCl$_3$): 19.34 (o-methyl), 21.12 (p-methyl), 128.6 (m), 132.9 (o), 136.30 (i), 140.9 (p), 170.5 (COCl) (lit.\textsuperscript{78} 19.32, 21.09, 128.6, 133.3, 136.4, 140.9, 170.43); solvent (benzene) appears at $\delta = 128.36$.

The literature standard method considered the unsubstituted benzene chemical shift as zero rather than 128.35 ppm determined with TMS standard and considering that the reported measurements was carried out in DMSO-$d_6$. All chemical shifts were in agreement with the literature values after adding 137.66 ppm for the
methylated carbons (which were reported relative to 1,3,5-tri-tert-butylbenzene) and 126.99 to the other carbons, i.e. the unsubstituted aromatic carbons (reported relative to benzene).\textsuperscript{78} \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta = 1.30$ (p-methyl), 1.44 (o-methyl), 7.4, 7.60, 8.21, 8.63.

\subsection*{3.4.3 (2,4,6-TRIMETHYLBENZOYL)DIPHENYLPHOSPHINE}

\begin{center}
\includegraphics[width=0.5\textwidth]{fig1.png}
\end{center}

$\textsuperscript{31}$P NMR (121 MHz, CDCl\textsubscript{3}): $\delta = 22.26$ ppm; $\textsuperscript{13}$C NMR (50 MHz, CDCl\textsubscript{3}): $\delta$ = 19.10, 21.17, 25.40, 67.70, 77.00, 125.08, 127.99, 128.09, 128.40, 128.80, 133.95, 137.56, 199.33 (carbonyl, d, 65 Hz), \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): $\delta = 1.86$ (p-methyl), 2.09 (o-methyl), 7.17, 7.20, 7.27, 7.29, 7.37 (benzene appears at 7.24 ppm).

\subsection*{3.4.4 (2,4,6-TRIMETHYLBENZOYL)DIPHENYLPHOSPHINE OXIDE (V)}

\begin{center}
\includegraphics[width=0.5\textwidth]{fig2.png}
\end{center}
$^{31}$P NMR (121 MHz, CDCl$_3$): $\delta = 11.43$ ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 19.51$, 21.02, 77.00, 128.43, 128.66, 128.71, 130.56, 131.62, 131.78, 132.18, 132.24, 134.71, 140.38, 219.92 (carbonyl, d, 72.5 Hz); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 2.05$ ($p$-methyl), 2.27 ($o$-methyl), 7.53, 7.81, 8.02, 8.21; IR 1664.90 cm$^{-1}$ (C=O), 1196.15 cm$^{-1}$ (P=O).

3.5 PROPOSED MECHANISM FOR THE SYNTHESIS OF bis(2,4,6-TRIMETHYLBENZOYL)PHENYLPHOSPHINE OXIDE (VI)

Synthesis of compound VI [bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide] was adapted from a patent, which starts with reduction of dichlorophenylphosphine to phenylphosphine. Acylation was performed in two steps using a stoichiometric amount of acyl halide and pyridine as base as shown in Figure 28. However, the final oxidation of the bis(2,4,6-trimethylbenzoyl)phenylphosphine to the oxide was not successful with either hydrogen peroxide or benzoyl peroxide oxidizing agents.

3.5.1 2,4,6-TRIMETHYLBENZOYL PHENYLPHOSPHINE

![Structure of 2,4,6-Trimethylbenzoyl Phenylphosphine](image)

$^{31}$P NMR (121 MHz, CDCl$_3$): $\delta = -18.85$ (d, 8 Hz). The $^{31}$P NMR spectrum after the first acylation reaction of phenylphosphine showed also phenylphosphine at
Figure 28. Mechanism for synthesis of \( \text{bis}(2,4,6\text{-trimethylbenzoyl})\)-phenylphosphine oxide (VI).
δ = –124.53, (tt, 200 and 7 Hz), which indicated that the reaction proceeded halfway and only one mesitoyl group added to the phenylphosphine.

3.5.2 *bis*(2,4,6-TRIMETHYLBENZOYL)PHENYLPHOSPHINE (VI)

![Chemical structure of bis(2,4,6-trimethylbenzoyl)phenylphosphine]

$^{31}$P NMR (121 MHz, CDCl$_3$): δ = 4.85 ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): δ = 19.63, 21.20, 67.70, 77.00, 126.67, 128.37, 128.59, 128.96, 132.08, 132.25, 132.83, 132.89, 135.23, 135.48, 136.07, 141.04, 181.25 (carbonyl, d, 60.0 Hz); $^1$H NMR (300 MHz, CDCl$_3$): δ = 1.66 ($p$-methyl), 2.27 ($o$-methyl), 7.55, 7.57, 7.87, 7.90 (benzene appears at 7.28 ppm).

3.6 METHOXYPHENYLPHOSPHINE OXIDE (VII)

![Chemical structure of methoxyphenylphosphine oxide]

$^{31}$P NMR (121 MHz, CDCl$_3$): (d of octets, δ = 25.43 ppm, 552.13 and 12.03 Hz); $^{13}$C NMR (50 MHz, CDCl$_3$): δ = 11.25, 26.60, 50.0, 51.82, 51.95, 77.00, 128.44, 128.71, 129.45, 130.51, 130.75, 132.99, 133.05; $^1$H NMR (300 MHz, CDCl$_3$): δ = 3.47, 3.50, 3.73 (d, 552 Hz), 6.528, 7.51, 7.53, 7.69, 7.71, 8.41
3.7  **p-TOLUOYLPHENYLPHOSPHINE OXIDE (IX)**

3.7.1  **p-TOLUOYLPHENYLPHOSPHINE**

\[
\text{CH}_3 - \text{C} - \text{P} - \text{O} - \text{C} - \text{O} - \text{CH}_3
\]

\[\begin{align*}
\text{31P NMR (121 MHz, CDCl}_3\text{): } \delta &= 10.78 \text{ ppm}; \\
\text{13C NMR (50 MHz, CDCl}_3\text{): } \delta &= 21.17, 21.65, 66.45, 77.00, 127.33, 128.61, 129.02, 129.19, 129.38, 129.71, 131.56, 132.95, 133.07, 133.19, 134.67, 135.04, 136.53, 137.23, 137.98, 143.59, 144.05, 211.89 \text{ (carbonyl, d, 36.64 Hz)};
\end{align*}\]

\[\begin{align*}
\text{1H NMR (300 MHz, CDCl}_3\text{): } \delta &= 1.94, 7.28, 7.38, 7.54 \text{ (d)}, 7.55, 7.58, 7.71, 8.09, 8.19, \text{ (benzene appears at 7.36 ppm)}
\end{align*}\]

3.7.2  **p-TOLUOYLPHENYLPHOSPHINE OXIDE (IX)**

\[
\text{CH}_3 - \text{C} - \text{P} - \text{O} - \text{C} - \text{O} - \text{CH}_3
\]

\[\begin{align*}
\text{31P NMR (121 MHz, CDCl}_3\text{): } \delta &= 20.56 \text{ ppm (pentet, 7.60 Hz)}; \\
\text{13C NMR (50 MHz, CDCl}_3\text{): } \delta &= 21.49, 128.02, 128.30, 128.53, 128.82, 129.17, 129.47, 130.23, 130.39, 131.32, 131.55, 131.74, 132.10, 137.57, 146.10, 146.55, 203.57 \text{ (carbonyl, d,}
\end{align*}\]

73
80 Hz); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 2.50, 7.56, 8.01, 8.06, 8.13, 8.58\) (benzene appears at 7.36 ppm).

3.8 (2,6–DIMETHOXYBENZOYL)DIPHENYLPHOSPHINE OXIDE (X)

3.8.1 2,6–DIMETHOXYBENZOYL CHLORIDE

\[
\begin{array}{c}
\text{OCH}_3 \\
\end{array}
\begin{array}{c}
\text{C} \\
\end{array}
\begin{array}{c}
\text{O} \\
\end{array}
\begin{array}{c}
\text{H} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\end{array}
\]

\(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 56.15, 56.24, 77.00, 103.96, 104.25, 132.08, 132.52, 156.15\) (carboxyl). For the anhydride, the carboxyl resonance appeared at 158.16 ppm \textit{versus} 165.98 ppm for the acid. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 4.57, 7.82, 7.97, 8.03, 8.26\) (benzene appears at 7.58 ppm).

3.8.2 (2,6–DIMETHOXYBENZOYL)DIPHENYLPHOSPHINE OXIDE (X)

\[
\begin{array}{c}
\text{CH}_3\text{O} \\
\end{array}
\begin{array}{c}
\text{O} \\
\end{array}
\begin{array}{c}
\text{O} \\
\end{array}
\begin{array}{c}
\text{CH}_3\text{O} \\
\end{array}
\]

\(^{31}\)P NMR (121 MHz, CDCl\(_3\)): \(\delta = 14.78\) (t, 9.87 Hz); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 21.17, 55.5, 55.67, 55.74, 77.00, 104.15, 111.71, 115.24, 125.33, 128.40, 128.18, 128.53, 128.82, 129.06, 130.25, 131.50, 131.55, 131.68, 131.93, 132.15, 132.25, 133.40, 137.54, 155.91, 158.05, 158.42, 211.15\) (carbonyl, d, 85.04 Hz); \(^1\)H
NMR (300 MHz, CDCl₃): δ = 3.60, 7.00, 7.11, 7.23, 7.72, 7.77 (benzene appears at 7.28 ppm); IR γ = 1695.10 cm⁻¹ (C=O), 1184.36 cm⁻¹ (P=O).

3.9  (PENTAFLUOROBENZOYL)DIPHENYLPHOSPHINE OXIDE (XI)

3.9.1  PENTAFLUOROBENZOIC ACID

![Chemical structure of Pentafluorobenzoic Acid]

$^{13}$C NMR (50 MHz, CDCl₃): δ = 137.87 ppm ($m$, $m$, $^1J_{C-F}$ = 259.4 Hz); 143.99 ($p$, $m$, $^1J_{C-F}$ = 261.6 Hz); 146.06 ($o$, $m$, $^1J_{C-F}$ = 260.09 Hz), 163.80 (carbonyl).

3.9.2  PENTAFLUOROBENZOYL CHLORIDE

![Chemical structure of Pentafluorobenzoic Acid]

$^{13}$C NMR (50 MHz, CDCl₃) δ = 137.80 ($m$, $m$, $^1J_{C-F}$ = 253.9 Hz); 144.37 ($p$, $m$, $^1J_{C-F}$ = 258.6 Hz); 144.43 ($o$, $m$, $^1J_{C-F}$ = 263.09 Hz); 112.50 ($i$, $m$), 158.13 (carboxyl, t, 2.5 Hz).
3.9.3 (PENTAFLUOROBENZOYL)DIPHENYLPHOSPHINE

\[
\begin{align*}
\text{\(3^1\text{P NMR (121 MHz, CDCl}\text{3): 26.65 ppm (tt, 41.06 and 7.60 Hz);}\)} \\
\text{\(13\text{C NMR (50 MHz, CDCl}\text{3): }\delta = 113.38, 129.48, 130.37, 133.73, 134.43, 141.50, 146.07, 209.14\) ppm (d, 42.03 Hz);} \\
\text{\(1^1\text{H NMR (300 MHz, CDCl}\text{3): }\delta = 7.54, 7.61, 7.68, 7.80, 7.82, 7.96.\)}
\end{align*}
\]

3.9.4 (PENTAFLUOROBENZOYL)DIPHENYLPHOSPHINE OXIDE (XI)

\[
\begin{align*}
\text{\(3^1\text{P NMR (121 MHz, CDCl}\text{3): }\delta = 17.98 \text{ (t, 7.60 Hz);}\)} \\
\text{\(13\text{C NMR (50 MHz, CDCl}\text{3): }\delta = 128.80, 129.76, 130.26, 132.030, 133.72, 134.43, 134.82, 139.95, 142.79, 144.74, 147.78, 209.14 \text{ (carbonyl, d, 86.04 Hz);}\)} \\
\text{\(1^1\text{H NMR (300 MHz, CDCl}\text{3): }\delta = 7.54, 7.61, 7.68, 7.80, 7.82;\)} \\
\text{\(\text{IR 1650.33 cm}^{-1} \text{ (C=O), 1123.67 cm}^{-1} \text{ (P=O).}\)}
\end{align*}
\]
3.10  (3,5-DINITROBENZOYL)DIPHENYLPHOSPHINE OXIDE (XII)

3.10.1  3,5-DINITROBENZOYL CHLORIDE

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O}_2\text{N} & \quad \text{Cl} \\
\text{O}_2\text{N} & \quad \text{O}_2\text{N}
\end{align*}
\]

$^{13}$C NMR (50 MHz, CDCl$_3$): $\delta = 124.19$, 130.27, 136.41, 148.89, 165.09; $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.69$ (p), 7.78 (o).

3.10.2  (3,5-DINITROBENZOYL)DIPHENYLPHOSPHINE

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O}_2\text{N} & \quad \text{C} \\
\text{O}_2\text{N} & \quad \text{P} \\
\text{O}_2\text{N} & \quad \text{O}_2\text{N}
\end{align*}
\]

$^{31}$P NMR (121 MHz, CDCl$_3$): $\delta = 14.86$ ppm; $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta =$ 121.75, 124.09, 127.40, 128.31, 129.34, 130.05, 130.52, 132.45, 141.44, 148.54, 209.98 ppm (carbonyl, d, 40.25 Hz); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.36$, 7.43, 7.47, 8.98.
3.10.3 PROPOSED REACTION MECHANISM OF SYNTHESIS OF (3,5-DINITROBENZOYL)DIPHENYLPHOSPHINE OXIDE (XII)

![Chemical Structure](image)

$^{31}$P NMR (121 MHz in CDCl$_3$): $\delta = 28.5$ and 35.6 ppm (dd, 846 and 22.89 Hz).

Various attempts at oxidation of the phosphine resulted in the formation of products other than the 3,5-dinitrobenzoyl)diphenylphosphine oxide, the desired product. Figures 29 and 30 propose possible mechanisms showing the formation of other possible compounds, such as a dinitro compound bearing two phosphorus groups. Formation of such products may be due to the strong electron withdrawing influence of the two nitro groups in positions three and five that inhibit the oxidation reaction. Upon oxidation of the (3,5-dinitrobenzoyl)diphenylphosphine with molecular oxygen, both the carbonyl carbon atom and the phosphorus could be attacked, forming benzoyl diphenylphosphinate which in turn is transformed into the anhydrides (PhCO)$_2$O and (Ph$_2$PO)$_2$. These results were in agreement with the literature concerning the mechanism of Arbuzov reaction for the nitro derivatives of acylphosphine oxides.$^{87,88}$
Figure 29. Proposed mechanism of the synthesis of (3,5-dinitribenzoyl)-diphenylphosphine oxide (Mech -1)
Figure 29 (continued). Proposed mechanism of the synthesis of (3,5-dinitrobenzoyl)diphenylphosphine oxide (Mech-1)
Figure 30. Proposed mechanism of the synthesis of (3,5-dinitribenzoyl)-diphenylphosphine oxide (Mech-2)
3.11 UV-VIS SPECTRAL ANALYSIS OF MONO- AND DI-ACYLPHOSPHINE OXIDES

The UV-VIS absorption spectrum of a two series of synthetic mono- and di-acylphosphine oxides was determined in acetonitrile. All solutions were prepared using acetonitrile (spectroscopic grade) purchased from Sigma-Aldrich and used as received for the solvent of 10 mM solutions with air as background. The maximum observed at between 300 to 500 nm, absorbance ($A$), and molar extinction coefficient $\varepsilon$ (M$^{-1}$ cm$^{-1}$) of each compound were determined.

Table 2. UV-VIS absorption spectra of mono- and di-acylphosphine oxides$^a$ at 25$^\circ$C

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda$ (nm)$^b$</th>
<th>$A$$^c$</th>
<th>$\varepsilon$ (M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoyldiphenylphosphine oxide</td>
<td>367</td>
<td>0.145</td>
<td>14.5</td>
</tr>
<tr>
<td>Dibenzoylphenylphosphine oxide</td>
<td>352 sh</td>
<td>0.159</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>367</td>
<td>0.808</td>
<td>80.8</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>1.001</td>
<td>100.1</td>
</tr>
<tr>
<td></td>
<td>395 sh</td>
<td>0.740</td>
<td>74.0</td>
</tr>
<tr>
<td>Benzoilmesitoylphenylphosphine oxide</td>
<td>369</td>
<td>1.35</td>
<td>135.0</td>
</tr>
<tr>
<td></td>
<td>390</td>
<td>1.05</td>
<td>105.0</td>
</tr>
<tr>
<td>Mesitoyldiphenylphosphine oxide</td>
<td>376 sh</td>
<td>1.36</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>391</td>
<td>1.663</td>
<td>166</td>
</tr>
<tr>
<td></td>
<td>406 sh</td>
<td>1.223</td>
<td>122</td>
</tr>
</tbody>
</table>

$^a$1 mM in acetonitrile in 1 cm cuvette.
$^b$Maximum absorption wavelength (sh = shoulder).
$^c$Baseline corrected absorbance.
Tables 2 and 3 summarize the UV-VIS data analysis for the series of the model compounds of benzoyldiphenyl-phosphine oxide and dibenzoyldiphenylphosphine oxide along with the mesitoyl derivatives of each compound prepared.

Table 2 summarizes the extinction coefficients for these compounds according to the Beer-Lambert law, \( \varepsilon = A / cl \) (where \( c \) is the molar concentration and \( l \) the pathlength in cm).

**Figure 31.** UV-VIS absorption spectra of mono- and di-acylphosphine oxides at 25° C

*\textit{bis}(2,6-Dichlorobenzoyl)phenylphosphine oxide*\(^{89}\) exhibits a maximum at 363 nm (\( \varepsilon = 113.0 \ M^{-1} \ cm^{-1} \)) in acetonitrile at room temperature, compared to that for dibenzoylphenylphosphine oxide at 367 nm (\( \varepsilon = 80.8 \ M^{-1} \ cm^{-1} \)). Under the same conditions, mesitoyldiphenylphosphine oxide exhibits a maximum at 391 nm (\( \varepsilon = 166.3 \ M^{-1} \ cm^{-1} \)).
M⁻¹ cm⁻¹) with two shoulders at 376 nm (ε 136.0 M⁻¹ cm⁻¹) and 406 nm (ε 122.3 M⁻¹ cm⁻¹), which agrees with Darcure-TPO from Ciba (which in dichloromethane has a maximum at 396 nm with ε = 179.3 M⁻¹ cm⁻¹ and two shoulders at 368 and 406 nm). The UV-VIS absorption spectra of the newly synthesized dibenzoylphenylphosphine oxide and benzoylmesitylphenylphosphine oxide were compared to benzoyl diphenylphosphine oxide in Figure 31.

**Table 3.** UV-VIS absorption spectra of monoacylphosphine oxides\(^a\) at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ (nm)(^b)</th>
<th>A(^c)</th>
<th>ε (M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoyldiphenylphosphine oxide</td>
<td>367</td>
<td>0.145</td>
<td>14.5</td>
</tr>
<tr>
<td>Mesityldiphenylphosphine oxide</td>
<td>376 sh</td>
<td>1.36</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>391</td>
<td>1.663</td>
<td>166.3</td>
</tr>
<tr>
<td></td>
<td>406 sh</td>
<td>1.223</td>
<td>122.3</td>
</tr>
<tr>
<td>(2,6-Dimethoxybenzoyl)diphenylphosphine oxide</td>
<td>(&gt;400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3,5-Dinitrobenzoyl)diphenylphosphine oxide</td>
<td>(&gt;400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Pentafluorobenzoyl)diphenylphosphine oxide</td>
<td>365</td>
<td>0.310</td>
<td>31.0</td>
</tr>
</tbody>
</table>

\(^a\)10 mM in acetonitrile in 1 cm cuvette.  
\(^b\)Maximum absorption wavelength (sh = shoulder).  
\(^c\)Baseline corrected absorbance.  
\(^d\)Absorption tailing > 400 nm.
indicating that the $\pi-\pi^*$ transitions can be found below 350 nm and the spin forbidden $n-\pi^*$ transitions (360-450 nm) have comparable low extinction coefficients, are responsible for the $\alpha$-cleavage and the formation of reactive radical sites in the dibenzoylphenylphosphine oxide. The two maxima found for dimesitylphenylphosphine oxide are due to different angles of the two carbonyl groups related to the P=O group. For (2,6-dimethoxybenzoyl)diphenyl phosphine oxide and (3,5-dinitrobenzoyldiphenyl)phosphine oxide, no absorption maxima were observed, and only tailing was seen beyond 400 nm.

### 3.12 PROPOSED REACTION MECHANISM FOR PHOTOLYSIS OF DIETHYL BENZOYLPHOSPHONATE

As a result of the exposure of diethyl benzoylphosphonate to 350 nm UV light, two free radicals are expected to form as a result of the cleavage of the C-P
bond. One radical will be carbon-centered and the other phosphorus-centered. These radicals are highly reactive and might recombine to form diethyl phosphoric anhydride and benzoin according to the mechanism in Figure 33. The $^{31}$P NMR spectroscopic analysis shown in Figure 131 indicates that diethyl phosphite also is formed (peaks 4), and two phosphorus-containing products (peaks 6 and 7) with chemical shifts of 21.9 ppm and 22.7 ppm are produced (P-O-P) which were found to be more deshielded than the diethyl benzoylephosphonate (peak 3). The chemical shifts reported in the literature$^{90}$ showed that diethyl phosphate [(C$_2$H$_5$O)$_2$P(O)OH. neat] in water had a chemical shift of zero, and the diethyl phosphoric anhydride [C$_2$H$_5$O)$_2$P(OP(O)(OC$_2$H$_5$)$_2$, neat] in solvent had a chemical shift of +13.4, which explain that the chemical shifts of these compounds varied for different solvents by 14 ppm. This possibility explains the formation of diethyl phosphoric anhydride [(C$_2$H$_5$O)$_2$P(OP(O)(OC$_2$H$_5$)$_2$] according to the mechanism proposed in Figure 33 and the assignment of the fragment ions in Table 9. The GC-MS spectroscopic analysis shown in Figures 140-144 indicates the formation of benzoin, diethyl phosphite, ethyl benzoate, and benzoic acid when compared with the standard mass spectra reported for these compounds.$^{91}$ Since the hydrolysis of diethyl benzoylphosphonate can result in the formation of these compounds except benzoin, the benzoin must be formed from the photolysis reaction.

3.13 $^{31}$P NMR- CHARACTERIZATION OF MONO- AND DI-ACYLPHOSPHINE OXIDES

Table 4 reports all the $^{31}$P NMR data for all the compounds prepared.
Chlorodiphenylphosphine ($^{31}$P NMR $\delta = 82.4$ ppm, t, $J = 7.6$ Hz) is reduced to phenylphosphine ($\delta = -124.6$ ppm), which appears as a triplet of triplets due to the two hydrogens atoms attached to phosphorus ($^{1}J_{PH} = 200$ Hz) and longer-range coupling with the two phenyl ortho H (6.8 Hz).
**Figure 33.** Proposed reaction mechanism of the photolysis of diethyl benzoylphosphonate
Figure 33 (continued). Proposed reaction mechanism of the photolysis of diethyl benzoylphosphonate

Dichlorophenylphosphine ($^{31}$P NMR $\delta = 161.06$ ppm, pentet, $J = 7.60$ Hz) is reduced to diphenylphosphine ($\delta = -42.60$ ppm), which appears as a doublet of pentets due to the coupling $^{1}J_{PH} = 102.0$ Hz and longer-range coupling with the four phenyl ortho H (6.8 Hz).

3.14 DIFFERENTIAL SCANNING CALORIMETRY RESULTS OF POLYMERIZATION OF MMA AND ACM WITH MONO- AND DI-ACYLPHOSPHINE OXIDES

Differential scanning calorimetry evaluated various monomers, synthetic Initiators as well as commercially inhibitors. The catalyst was benzoyl peroxide from Sigma Aldrich and was used as received, and the synthetic initiators were mono- and di-acylphosphine oxides. The monomers were methyl methacrylates
Table 4. $^{31}$P NMR characterization of mono- and di-acylphosphine oxides

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta^{31}$P (ppm)</th>
<th>J (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorodiphenylphosphine</td>
<td>82.42 (t)</td>
<td>7.63</td>
</tr>
<tr>
<td>Methoxydiphenylphosphine</td>
<td>115.75 (octet)</td>
<td>8.00</td>
</tr>
<tr>
<td>Diphenylphosphine</td>
<td>-42.60 (dt)</td>
<td>102.00, 7.63</td>
</tr>
<tr>
<td>Benzyldiphenylphosphine</td>
<td>11.20 (t)</td>
<td></td>
</tr>
<tr>
<td>Benzyldiphenylphosphine Oxide</td>
<td>21.89 (pentet)</td>
<td></td>
</tr>
<tr>
<td>Dichlorophenylphosphine</td>
<td>161.06 (t)</td>
<td>7.60</td>
</tr>
<tr>
<td>Phenylphosphine</td>
<td>-124.64 (tt)</td>
<td>200.00, 7.00</td>
</tr>
<tr>
<td>Dibenzoylphenylphosphine</td>
<td>28.82 (pentet)</td>
<td></td>
</tr>
<tr>
<td>Dibenzoylphenylphosphine Oxide</td>
<td>18.29 (pentet)</td>
<td>4.55</td>
</tr>
<tr>
<td>(2,4,6-Trimethylbenzoyl)diphenylphosphine</td>
<td>22.26</td>
<td></td>
</tr>
<tr>
<td>(2,4,6-Trimethylbenzoyl)diphenylphosphine Oxide</td>
<td>11.43</td>
<td></td>
</tr>
<tr>
<td>Toluoyldiphenylphosphine</td>
<td>10.78</td>
<td></td>
</tr>
<tr>
<td>Toluoyldiphenylphosphine Oxide</td>
<td>20.58</td>
<td></td>
</tr>
<tr>
<td>bis(2,4,6-Trimethylbenzoyl)phenylphosphine</td>
<td>4.83</td>
<td></td>
</tr>
<tr>
<td>Methoxyphenylphosphine Oxide</td>
<td>25.43 (d of heptets)</td>
<td>552.10, 13.9</td>
</tr>
<tr>
<td>(2,6-Dimethoxybenzoyl)diphenylphosphine Oxide</td>
<td>14.77 (t)</td>
<td>9.87</td>
</tr>
<tr>
<td>(3,5-Dinitrobenzoyl)diphenylphosphine</td>
<td>14.86</td>
<td></td>
</tr>
<tr>
<td>(3,5-Dinitrobenzoyl)diphenylphosphine Oxide</td>
<td>21.07</td>
<td></td>
</tr>
<tr>
<td>(3,5-Dinitrobenzoyl)diphenylphosphine Oxide (Isomerization )</td>
<td>28.5, 35.6 (dd)</td>
<td>153.13, 22.89</td>
</tr>
<tr>
<td>(Pentafluorobenzoyl)diphenylphosphine Oxide</td>
<td>26.65 (tt)</td>
<td>41.06, 7.60</td>
</tr>
<tr>
<td>(Pentafluorobenzoyl)diphenylphosphine Oxide</td>
<td>17.98 (t)</td>
<td>7.60</td>
</tr>
</tbody>
</table>

and acrylamide from Sigma Aldrich and were used as received at concentrations of 90/10 (wt) monomer/initiator. DSC was performed per the following conditions: heating rate 10° C/min, nitrogen flow of 60 mL/min., heating range from 0-160° C, and sample size 10 mg. All of the mass and thermal analysis conditions were
standardized as describe above. Thermal Solutions® software was used to analyze the DSC curves.

![Methyl methacrylates](image1.png) ![Acrylamide](image2.png)

**Figure 34.** Model monomers used for the polymerization with mono- and di-acylphosphine oxides

The monomer acrylamide and the benzoyl peroxide catalyst were used as model chemical substrates. They were examined separately plus in combination. Acrylamide endothermically melted at 84.0°C with a heat of fusion of 133 J/g. ACM then exothermically autopolymerized at 119°C in nitrogen (literature ACM 133°C in air, plus diacetone acrylamide autopolymerized at 118°C in nitrogen and 130°C in air). The average activation energy for diacetone-acrylamide polymerization was 51.1±3.0 kcal/mole. This should be approximately the same for ACM. Inhibitors increased the activation energy to 64 kcal/mol for p-methoxyphenol and 134 kcal/mol for 4-tert-butylpyrocatechol. Therefore, the addition of a catalyst must drop the activation energy below 51 kcal/mole. The heat of polymerization observed was 41.9 J/g (Literature ACM 50.0 J/g). Next, benzoyl peroxide was scanned and decomposed rendering free radicals at 112°C with an exothermic heat of 411 J/g. Combination of the monomer and catalyst 90/10 (wt) respectively, caused the acrylamide to
significantly polymerize at 91°C with an exotherm of 411 J/g, a five-fold increase in the anticipated heat of polymerization.

Figure 35 explain the relative rate of polymerization (314 W/g/min for benzoyl peroxide, 788 for the ACM/catalyst, and only 13 for ACM alone). The model system (ACM and the catalysts) behaved appropriately and the DSC tracked the endothermic and exothermic events.

![Derivative heat flow vs. time/temperature of benzoyl peroxide by DSC](image)

**Figure 35.** Derivative heat flow vs. time/temperature of benzoyl peroxide by DSC

Derivative heat flow vs. time/temperature from a temperature scanned DSC of the polymerization of benzoyl peroxide (BP) and an acrylamide (ACM) monomer, the relative rate of polymerization of ACM/BP is greatly enhanced to 790 W/g/min.

The melting properties of mono- and di-acylphosphine oxides are summarized in the Table 5. Triplicate DSC melting curves differentiated the two catalysts, that is,
the average mono melting temperatures were 90-94°C with a heat of fusion of 49 J/g. The average bis melting temperatures were 132-135°C with a heat of fusion of 92 J/g, the sharp melting over a 3-4°C range is a measure of a pure compound. Acylphosphine oxides are known to catalyze monomer polymerization by generating multiple free radicals. For example, (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (364 g/mole) generates two free radicals, and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (416 g/mole) three free radicals. The melting temperatures

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Melt Temperature (°C)</th>
<th>Peak Melt Temperature (°C)</th>
<th>Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoacylphosphine Oxide</td>
<td>92</td>
<td>94</td>
<td>49.4</td>
</tr>
<tr>
<td>Diacylphosphine Oxide</td>
<td>132</td>
<td>135</td>
<td>92.5</td>
</tr>
</tbody>
</table>

Table 5. The average DSC melting properties of the mono- and di-acylphosphine oxide in triplicate

Table clearly and statistically differentiate the two initiators, and the differentiated catalysts
samplings was three.

The DSC polymerization was a two step process and the peak temperatures were discovered at 26° and 54°C for the diacylphosphine oxide, and 36° and 54°C for the monoacylphosphine oxide (see Figure 36 and Table 6). The two step DSC relative polymerization rate of the two acylphosphine oxide catalysts and the monomer methyl methacrylates, and the relative polymerization rate is the ratio of the diacylphosphine oxide rate divided by the monoacylphosphine oxide rate, Table 7 and
it indicates that the diacylphosphine oxide is 18% faster than the monoacylphosphine oxide. The relative reaction rates for both initiators for a two step process were: 107 and 89 mW/g/min and 90 and 76 mW/g/min, respectively. The ratio of free radicals formed for the two phosphine oxides is 1.5 or 3.0. The total DSC energy (mW/g) associated with the two step polymerization process was 1.55 or 3.10. This structure of the synthetic initiators, the number of free radicals formed and property (DSC two step polymerization energy) relationship is repeatably valid and is related to the polymerization mechanism (see Figure 37 and Tables 7 and 8). The relative polymerization rate is the ratio of the di-rate divided by the mono rate.

**Figure 36.** Polymerization in the DSC of acylphosphine oxide catalysts and the monomer methyl methacrylate.
Table 6. DSC heat of polymerization of the mono-and di-acylphosphine oxide with methyl methacrylates.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Temperature °C (Step 1)</th>
<th>Temperature °C (Step 2)</th>
<th>Heat of Polymerization J/g J/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono(acyl)phosphine oxide</td>
<td>40</td>
<td>57</td>
<td>5.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2200</td>
</tr>
<tr>
<td>Di-(acyl)phosphine oxide</td>
<td>29</td>
<td>57</td>
<td>5.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2400</td>
</tr>
</tbody>
</table>

Figure 37. The two step DSC relative polymerization rate of the two acylphosphine oxide catalysts and the monomer methyl methacrylates.
**Table 7.** DSC relative polymerization rate of mono- and di-acylphosphine oxide with methyl methacrylate.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Polymerization Rate (mW/g/min) (Step 1)</th>
<th>Polymerization Rate (mW/g/min) (Step 2)</th>
<th>Relative Polymerization Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoacylphosphine oxide</td>
<td>90</td>
<td>76</td>
<td>=100</td>
</tr>
<tr>
<td>Diacylphosphine oxide</td>
<td>107</td>
<td>89</td>
<td>118</td>
</tr>
</tbody>
</table>

**Table 8.** DSC polymerization heat rate of of mono-and di-acylphosphine oxide with methyl methacrylates.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Heat/Rate Curve (mW/g) (Step 1)</th>
<th>Heat/Rate Curve (mW/g) (Step 2)</th>
<th>Heat Ratio (Di/Mono) Ratio Free Radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoacylphosphine oxide</td>
<td>51</td>
<td>24</td>
<td>=75</td>
</tr>
<tr>
<td>Diacylphosphine oxide</td>
<td>41</td>
<td>75</td>
<td>=116</td>
</tr>
</tbody>
</table>

The relative heat ratio from the derivative DSC curves is the sum of the heats for each catalyst.
CHAPTER IV

CONCLUSION

Understanding the chemical and the physical properties of existing initiators increased research on the preparation of the model compound of these initiators. For the same purpose, benzoyl diphenylphosphine oxide (I) was synthesized for the first time in a two step reaction process starting from chlorodiphenylphosphine with a 90% overall yield, of bright white crystals. The $^1$H, $^{13}$C, and $^{31}$P NMR, and the UV-VIS spectroscopic data, were in agreement. Following the same strategy of the synthesis a series of monoacylphosphines and their corresponding oxides were synthesized, the primary goal of these series of compounds was to explore a new route of their synthesis which have not been reported, except in patents. The spectroscopic properties of these compounds i.e. $^{31}$P NMR, $^{13}$C NMR, and $^1$H NMR was reported for the first time as well as the IR spectroscopy of some of these compounds. GC-mass spectra for the phosphine oxides was not successful due to the bulky groups on the carbonyl species but it was successful for the benzoyldiethylphosphonate since it was so bulky and less reactive than the oxides.
Our series of monoacylphosphine oxides include toluoyldiphenylphosphine oxide, mesitoyldiphenylphosphine oxide (2,6-dimethoxybenzoyl)diphenylphosphine oxide, (pentafluorobenzoyl)diphenylphosphine oxide and (3,5-dinitrobenzoyl)-diphenylphosphine the oxide derivative of this compound was not successful due to the dimerization of the (pentafluorobenzoyl)diphenylphosphine during the oxidation because of the electronic effect of the two electron withdrawing groups at position 3 and 5 of the benzoyl group.

Dibenzoylphenylphosphine oxide (II) was first synthesized as a model compound for the synthesis of a new series of diacylphosphines and diacylphosphine oxides, this compound was reported for the first time. The synthesis of the diacylphosphine oxides was more difficult than the acylphosphine oxides because of the steric hindrance of the bulky groups which was introduced to enhance stability and solubility of these initiators to be used in aqueous media. The acylation of the phenylphosphine was in two step mechanism first acylation was always easy step, but thee second acylation was too difficult to achieve with more sterically hindered acid chlorides.

The study of the polymerization using the two model photoinitiators i.e. mono- and di-acylphosphine oxides with model monomer acrylamide and methyl methacrylates was carried out at the DSC polymerization reactor and revealed that the methyl methacrylates monomer polymerizes in a two step reaction with either synthesized phosphine oxide. Diacylphosphine oxide is more reactive than monoacylphosphine oxide by 18% as measured by DSC. The ratio of the heat measurement from the DSC reactivity study was 1.55 or 3.10 and the ratio of the
number of known free radicals Di/Mono = 3/2=1.5 or 3.00. There is a repeatably good structure (ratio of known free radicals) and property (DSC measurement of total heat in the reactivity study) relationship for the acylphosphosphine oxides. There was no apparent difference in the heat of polymerization of the two initiators with methyl methacrylates.

Future research would be to investigate the same class of photoinitiators and will focus on using the derivatives of compound I which has a more steric hindered structure, like diethyl (trimethylbenzoyl)phosphonate and the as well as a moisture-free reaction condition to avoid hydrolysis. Further research will be to irradiate the system with UV light in the presence of a monomer, such as ethylene glycol or propylene. Future More work on the synthesis and characterization of the derivatives of mono- and di-acylphosphine oxide, the main goal is to increase the steric hindrance near the benzoyl group in order to stabilize the initiators toward hydrolysis. (4-Methoxy-2,6-dimethylbenzoyl)diphenylphosphine oxide and bis(4-methoxy-2,6-dimethylbenzoyl)phenylphosphine oxide will be prepared according to Michaelis–Arbuzov reaction as adapted from a patent. The influence of the structure modification on the stability and solubility of these compounds in aqueous media by the introduction of the methoxy (hydrophilic) group in the para position, and two methyl groups in the ortho positions of the benzoyl moiety. The photochemical reactivity of these photoinitiators will be addressed using and vinyl acrylate monomers as model substrates for the free radical polymerization process. The chemical properties of the polymers, including the degree of polymerization, the distribution of co-monomers, the incorporation of the unsaturated end groups, and the
degree of crosslinking of the end groups, using nuclear magnetic resonance, infrared,
gas chromatography-mass spectra and UV-VIS absorption spectroscopic techniques. The mechanical and rheological properties of the polymers also will be investigated by appropriate techniques, such as thermogravimetric analysis.

The mechanism of the free radical polymerization of these photoinitiators will be studied in order to provide a better understanding of the compatibility of these compounds for their application in clinical dentistry. Also a noble metal will be employed in the process to form the desired composite scaffold. Possible in vivo testing of the performance of the synthetic polymers by collaboration with clinicians at the Case Western Reserve University School of Dentistry.
APPENDIX A

Compilation of $^1$H, $^{13}$C, and $^{31}$P NMR Spectra
Figure 38. $^{31}P$ NMR spectrum of chlorodiphenylphosphate in CDCl$_3$.

Figure 39. $^{13}C$ NMR (left) and $^1H$ NMR (right) spectra of chlorodiphenylphosphate in CDCl$_3$. 
Figure 40. $^1$H NMR spectrum of $N,N$-diethylaniline.

Figure 41. $^{13}$C NMR spectrum of $N,N$-diethylaniline in CDCl$_3$. 
Figure 42. $^{13}$C NMR spectrum of benzoyl chloride in CDCl$_3$.

Figure 43. $^1$H NMR spectrum of benzoyl chloride in CDCl$_3$. 
Figure 44. $^{31}$P NMR spectrum of methoxydiphenylphosphine in CDCl$_3$. 
Figure 45. $^{13}$C NMR spectrum of methoxydiphenylphosphine in CDCl$_3$. 
Figure 46. $^1$H NMR spectrum of methoxydiphenylphosphine in CDCl$_3$, $\delta = 3.76$ ppm for the methoxy group coupled to phosphorus (after evaporation of the solvent).
Figure 47. $^{31}$P NMR spectrum of diphenylphosphine in CDCl$_3$, $\delta$ = -42.6 (dt, $J = 102.0$ and 7.63 Hz).
Figure 48. $^{13}$C NMR spectrum of diphenylphosphine in CDCl$_3$. 
Figure 49. $^1$H NMR spectrum of diphenylphosphine in CDCl$_3$. 
Figure 50. $^{31}$P NMR spectrum of benzoyldiphenylphosphine in CDCl$_3$, $\delta$ = 11.2 ppm
Figure 51. $^{13}$C NMR spectrum of benzoyldiphenylphosphine in CDCl$_3$. 
Figure 52. $^1$H NMR spectrum of benzyldiphenylphosphine in CDCl$_3$. 
Figure 53. $^{31}$P NMR spectrum of benzoyldiphenylphosphine oxide (I), $\delta = 21.89$ (pentet), after recrystallization from ethyl acetate.
Figure 54. $^{13}$C NMR spectrum of benzoyle diphenyl phosphine oxide (I)
Figure 54.(continued) $^{13}$C NMR spectrum of benzoyldiphenylphosphine oxide (I) showed 8 peaks in the region $\delta = 128$-141 ppm for the aromatic carbons and a low field resonance at $\delta = 196.72$ for the carbonyl carbon.
Figure 55. $^1$H NMR spectrum of benzoyldiphenylphosphine oxide (II)
Figure 56. $^{31}$P NMR spectrum of dichlorophenylphosphine in CDCl$_3$, $\delta = 161.06$ ppm
Figure 57. $^{13}$C NMR spectrum of dichlorophenylphosphine in CDCl$_3$
Figure 58. $^1$H NMR spectrum of dichlorophenylphosphine in CDCl$_3$
Figure 59. $^{31}$P NMR spectrum of phenylphosphine in CDCl$_3$, $\delta$ = -124.53 (tt, $J = 200$ and 7 Hz.)
Figure 60. $^{13}$C NMR spectrum of phenylphosphine in CDCl$_3$
**Figure 61.** $^1$H NMR spectrum of phenylphosphine in CDCl$_3$
Figure 62. $^{31}$P NMR spectrum of dibenzoylphenylphosphine in CDCl$_3$, $\delta = 28.82$ ppm
Figure 63. $^{13}$C NMR spectrum of dibenzoylphenylphosphine in CDCl$_3$
Figure 64. $^1$H NMR spectrum of dibenzoylphenylphosphine in CDCl$_3$
Figure 65. $^{31}$P NMR spectrum of dibenzoylphenylphosphine oxide in CDCl$_3$, $\delta =$ 18.29 ppm
Figure 66. $^{13}$C NMR spectrum of dibenzoylphenylphosphine oxide in CDCl$_3$
Figure 67. $^1$H NMR spectrum of dibenzoylphenylphosphine oxide in CDCl$_3$
Figure 68. $^{13}$C NMR spectrum of pyridine in CDCl$_3$ 

Figure 69. $^1$H NMR spectrum of pyridine in CDCl$_3$
Figure 70. $^{13}$C NMR spectrum of mesitoic acid (2,4,6-trimethylbenzoic acid), the characteristic C=O carbonyl group $\delta = 175.7$ ppm
Figure 71. $^{13}\text{C}$ NMR spectrum of mesitoyl chloride (2,4,6-trimethylbenzoyl chloride) the characteristic C=O carbonyl group $\delta = 170.5$ ppm.
Figure 72. $^1$H NMR spectrum of mesitylchloride (2,4,6-trimethylbenzoyl chloride)
Figure 73. $^{13}$C NMR spectrum of mesitoic anhydride (2,4,6-trimethybenzoic anhydride)
Figure 74. $^{31}$P NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphosphine $\delta =$ 22.26 ppm
Figure 75. $^{13}$C NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphosphine
Figure 76. $^1$H NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphosphine
Figure 77. $^{31}\text{P}$ NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide $\delta = 11.43$ ppm
Figure 78. $^{13}$C NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide
Figure 79 $^1$H NMR spectrum of (2,4,6-trimethylbenzoyl)diphenylphospine oxide
Figure 80. $^{13}$C NMR spectrum of toluoyl chloride in CDCl$_3$
Figure 81. $^1$H NMR spectrum of toluoyl chloride
**Figure 82.** $\text{^{31}P}$ NMR spectrum of toluoyldiphenylphosphine $\delta = 10.78$ ppm
Figure 83. $^{13}$C- NMR spectrum of toluoyldiphenylphosphine
Figure 84. $^1$H NMR spectrum of toluoyldiphenylphosphine
Figure 85. $^{31}$P NMR spectrum of toluoyldiphenylphosphine oxide $\delta = 20.58$ ppm
Figure 86. $^{13}$C NMR spectrum of toluoyldiphenylphosphine oxide
Figure 86(continued). $^{13}$C- NMR spectrum of toluoyldiphenylphosphine oxide
Figure 87. $^1$H NMR spectrum of toluoyldiphenylphosphine oxide
Figure 88. $^{31}$P NMR spectrum of phenylphosphine in CDCl$_3$, $\delta$ = -124.53, ($tt$, $J$ = 200, 7 Hz) and (2,4,6-trimethylbenzoyl)phenylphosphate $\delta$ = -18.85 ($d$, $J$ = 8 Hz)
Figure 89. $^{13}$C NMR spectrum of (2,4,6-trimethylbenzoyl)phenylphosphine in CDCl$_3$. 
Figure 90. $^1$H NMR spectrum of (2,4,6-trimethylbenzoyl)phenylphosphine in CDCl$_3$. 
Figure 91. $^{31}$P NMR spectrum of $bis(2,4,6$-trimethylbenzoyl)$phenylphosphine
Figure 92. $^{13}$C NMR spectrum of bis(2,4,6-trimethylbenzoyl)phenylphosphine in CDCl$_3$. 
Figure 93. $^1$H NMR spectrum of bis(2,4,6-trimethylbenzoyl)phenylphosphine in CDCl$_3$. 
Figure 94. $^{31}$P NMR spectrum of methoxyphenylphosphine oxide, ($d$, $P\delta = 25.43$ ppm, $J = 552$ Hz)
Figure 95. $^{13}\text{C}$ NMR spectrum of methoxyphenylphosphine oxide in CDCl$_3$. 
Figure 96. $^1$H NMR spectrum of methoxyphenylphosphine oxide in CDCl$_3$
**Figure 97.** $^{13}$C NMR spectrum of 2,6-dimethoxybenzoyl chloride in CDCl$_3$
Figure 98. $^1$H NMR spectrum of 2,6-dimethoxybenzoyl chloride in CDCl$_3$
Figure 99. $^{31}$P- NMR spectrum of (2,6-dimethoxybenzoyl)diphenylphosphine oxide
Figure 100. $^{13}$C NMR spectrum of (2,6-dimethoxybenzoyl)diphenylphosphine oxide
Figure 101. $^1$H NMR spectrum of 2,6-dimethoxybenzoyldiphenylphosphine oxide
Figure 102. $^{13}$C NMR spectrum of 3,5-dinitrobenzoyl chloride in CDCl$_3$
Figure 103. $^1$H NMR spectrum of 3,5-dinitrobenzoyl chloride in CDCl$_3$
Figure 104. $^{31}$P- NMR spectrum of 3,5-dinitrobenzoylphenylphosphine in CDCl$_3$, $\delta = 4.86$ ppm
Figure 105. $^{13}$C NMR spectrum of 3,5-dinitrobenzoydiphenylphosphine in CDCl$_3$
Figure 106. $^1$H NMR spectrum of 3,5-dinitrobenzoydiphenylphosphine in CDCl$_3$. 

![Chemical Structure](image.png)
**Figure 107.** $^{31}$P-NMR spectrum of 3,5-dinitrobenzoyl diphenylphosphine Oxide
Figure 108. $^{31}$P- NMR spectrum of dimerization product 3,5-Dinitrobenzyl-di(diphenylphosphine oxide) in CDCl$_3$ (d,d $\delta = 28.5, 35.6$ ppm, $J = 23$ Hz)
Figure 108 (continued). $^{31}$P-NMR spectrum of 3,5-Dinitrobenzyl-di(diphenylphosphine) oxide
Figure 109. $^{13}$C NMR spectrum of pentafluorobenzoic acid in CDCl$_3$
Figure 110. $^1$H NMR spectrum of pentafluorobenzoic acid in CDCl$_3$
Figure 111. \(^{13}\)C NMR spectrum of pentafluorobenzoic acid in CDCl\(_3\)
Figure 112. $^1$H NMR spectrum of pentafluorobenzoic acid in CDCl$_3$
Figure 113. $^{31}$P- NMR spectrum of pentafluorobenzoyldiphenylphosphine in CDCl$_3$
Figure 114. $^{13}$C NMR spectrum of pentafluorobenzoxyldiphenylphosphine in CDCl$_3$
Figure 114 (continued). $^{13}$C NMR spectrum of Pentafluorobenzoyl-diphenylphosphine in CDCl$_3$
Figure 115. $^1$H NMR spectrum of pentafluorobenzoyldiphenylphosphine in CDCl$_3$
Figure 116. $^{31}$P- NMR spectrum of pentafluorobenzoyldiphenylphosphine oxide in CDCl$_3$
Figure 117. $^{13}$C NMR spectrum of Pentafluorobenzoyldiphenylphosphine oxide in CDCl$_3$
Figure 117(continued). $^{13}$C NMR spectrum of pentafluorobenzoyl-diphenylphosphine oxide in CDCl$_3$
Figure 118. $^1$H NMR spectrum of pentafluorobenzoylefdiphosphine oxide in CDCl$_3$
Figure 119. $^{31}$P- NMR spectrum of triphenylphosphine in CDCl$_3$, $\delta$ = -7.37 ppm
Figure 120. $^{13}$C NMR spectrum of triphenylphosphine in CDCl$_3$
Figure 121. $^1$H NMR spectrum of triphenylphosphine in CDCl$_3$
**Figure 122.** $^{31}$P- NMR spectrum of triphenylphosphine oxide in CDCl$_3$, $\delta = 27.36$ ppm
Figure 123. $^{13}$C NMR spectrum of triphenylphosphine oxide in CDCl$_3$
Figure 124. $^1$H NMR spectrum of triphenylphosphine oxide in CDCl$_3$
Figure 125. $^{13}$C NMR spectrum of anhydrous toluene in CDCl$_3$
(CH₃CH₂O)₃P

Figure 126. $^{31}$P NMR spectrum of triethyl phosphite in CDCl₃.
Figure 127. $^{13}$C NMR spectrum of triethyl phosphite.
Figure 128. $^1$H NMR spectrum of triethyl phosphite.
Figure 129. $^{31}P$ NMR spectrum of diethylbenzoylphosphonate in CDCl$_3$. 
Figure 130. $^{13}$C NMR spectrum of diethylbenzoylphosphonate in CDCl$_3$. 
Figure 131. $^{31}$P NMR spectra of diethyl benzoylphosphonate (peaks 3) in ethyl acetate after irradiation by a sun lamp for 60, 120 (proton coupled), and 240 min. Diethylphosphite (peaks 4) was formed and four phosphorus containing compounds were also formed (peaks 1,2,5,6).  Spectrum in CDCl$_3$. 
Figure 132. $^{13}$C NMR spectrum of diethylbenzoylphosphonate in CDCl$_3$ in ethyl acetate, after 240 min. irradiation. Benzoic acid (peaks 4), ethyl benzoate (peaks 3) and diethyl phosphite (peaks 1) were formed ($x = $ solvent).
Figure 132 (continued). $^{13}$C NMR spectrum of diethyl benzoylphosphonate dissolved in acetonitrile after 240 min. irradiation. Benzoic acid (peaks 3), diethyl phosphite (peaks 1) and benzoin (peaks 5) were formed.
**Figure 133** $^{31}$P NMR spectra of the irradiation reaction of $bis(2,4,6$-trimethylbenzoyl)$phenylphosphine$ oxide, after 30 min photolysis.
Figure 133 (continued) The irradiation reaction of *bis*(2,4,6-trimethylbenzoyl)phenylphosphine oxide after 60, 120 min photolysis.
APPENDIX B

Compilation of IR- Spectra of Selected Acylphosphine oxides Compounds
2,4,6-Trimethylbenzoyldiphenyl phosphine oxide

**Figure 134.** IR spectra of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (γ = 1664.90 cm⁻¹ C=O, 1196.15 cm⁻¹ P=O)
2,6-Dimethoxybenzoyldiphenylphosphine oxide

**Figure 135.** IR spectra of 2,6-dimethoxybenzoyldiphenylphosphine oxide ($\gamma = 1695.10$ cm$^{-1}$ C=O, 1184.36 cm$^{-1}$ P=O)
Figure 136 IR spectra of pentafluorobenzoyldiphenylphosphine oxide ($\gamma = 1650.33 \text{ cm}^{-1} \text{ C}=\text{O}, 1123.67 \text{ cm}^{-1} \text{ P}=\text{O}$)
APPENDIX C

Compilation of GC - Mass Spectra Data
**Table 9.** Assignments for fragment ions of diethyl benzoylphosphonate in acetonitrile after irradiation for 4 hrs.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>m/z</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9</td>
<td>M+1 = 139</td>
<td>[Diagram of PHOOOH]</td>
</tr>
<tr>
<td></td>
<td>D+1 = 111</td>
<td>[Diagram of POOOH]</td>
</tr>
<tr>
<td></td>
<td>D = 83</td>
<td>H4PO3+</td>
</tr>
<tr>
<td></td>
<td>D = 65</td>
<td>H2PO2+</td>
</tr>
<tr>
<td>9.18</td>
<td>M = 122</td>
<td>[Diagram of benzoic acid]</td>
</tr>
<tr>
<td></td>
<td>D = 105</td>
<td>[Diagram of benzylaldehyde]</td>
</tr>
<tr>
<td></td>
<td>D = 77</td>
<td>[Diagram of phenyl]</td>
</tr>
<tr>
<td>Time (min)</td>
<td>m/z</td>
<td>ion</td>
</tr>
<tr>
<td>-----------</td>
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<td>----------------------</td>
</tr>
<tr>
<td>9.49</td>
<td>M = 150</td>
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<td></td>
<td>D = 122</td>
<td>benzonic acid</td>
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<td></td>
<td>D = 105</td>
<td>benzyl aldehyde</td>
</tr>
<tr>
<td>10.91</td>
<td>M = 212</td>
<td>phenyl</td>
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</table>

Benzoin
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<th>Time (min)</th>
<th>m/z</th>
<th>ion</th>
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</thead>
<tbody>
<tr>
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<td></td>
<td>benzyl aldehyde</td>
</tr>
<tr>
<td></td>
<td></td>
<td>phenyl</td>
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</tbody>
</table>

D = 105

D = 77
Table 10. Relative abundance of diethyl benzoylphosphonate in acetonitrile after irradiation for 4 hrs.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>analyte</th>
<th>m/z</th>
<th>relative abundance</th>
</tr>
</thead>
<tbody>
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<td>5.9</td>
<td>diethyl phosphite</td>
<td>139</td>
<td>4 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111</td>
<td>52 %</td>
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<tr>
<td></td>
<td></td>
<td>83</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>65</td>
<td>75 %</td>
</tr>
<tr>
<td>9.18</td>
<td>benzoic acid</td>
<td>122</td>
<td>68 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105</td>
<td>100 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>77</td>
<td>88 %</td>
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<tr>
<td>9.49</td>
<td>ethyl benzoate</td>
<td>150</td>
<td>13 %</td>
</tr>
<tr>
<td></td>
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<td>25 %</td>
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<td>100 %</td>
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<td></td>
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<td>88 %</td>
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<tr>
<td>10.9</td>
<td>benzoin</td>
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<td>107</td>
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<td>77</td>
<td>100 %</td>
</tr>
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</table>
Diethyl benzoylphosphonate

\[
\text{\begin{align*}
&\text{\begin{array}{c}
\text{O} \\
\text{C} \\
\text{P} \\
\text{OCH}_2\text{CH}_3 \\
\text{OCH}_2\text{CH}_3
\end{array}}
\end{align*}}
\]

Figure 137. Mass chromatogram of diethyl benzoylphosphonate

Figure 138. Mass spectrum of diethyl benzoylphosphonate (m/z = 242)
**Figure 139.** Chromatogram (TIC) of diethyl benzoylphosphonate in acetonitrile after exposure to sun lamp for 30 and 120 min

**Figure 140.** GC chromatogram of diethyl benzoylphosphonate in acetonitrile after irradiation for 4 hrs. to sun lamp; one new peak detected at 10.9 min (benzoin)
Diethyl phosphite

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{P} \quad \text{OCH}_2\text{CH}_3 \\
\text{OCH}_2\text{CH}_3
\end{array}
\]

Figure 141. Mass spectrum at 5.9 min, diethyl phosphite (\(M^+ = 138\) m/z). (top Experimental, bottom Standard)
Figure 142. Mass spectrum of benzoic acid (M$^+$ = 122 m/z). (top Experimental, Bottom Standard)
Figure 143. Mass spectra at 9.48 min, ethyl benzoate (M$^+$ = 150 m/z)
Figure 143(continued). Mass spectrum of ethyl benzoate.$^{30}$
Figure 144. Mass spectra at 10.91 min, benzoin (M⁺ = 212 m/z).
**Figure 144 (continued)** Standard mass spectrum of benzoin.\textsuperscript{31}
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