Chapter 2

Design, synthesis and application of novel benzil derivatives as photostabilizers for Chlorpyrifos
2.1 Abstract

Design and synthesis of novel benzil derivatives is reported and furthermore, they are employed as photostabilizers to study the photostabilization of chlorpyrifos under UV light. The percentage recovery of chlorpyrifos after UV irradiation is obtained by HPLC. Results indicate significant enhancement in the photostabilization of chlorpyrifos using these benzil derivatives in comparison with 2,4-dihydroxy benzophenone, a reference photostabilizer.
2.2 Introduction

The sunlight emits broad range of electromagnetic radiations such as gamma rays to radio waves. The sunlight plays an important role in the routine life processes of living organisms on the earth by providing energy in the form of light such as plant photosynthesis and production of Vitamin D in the human body. In spite of its importance, it is also causing serious adverse effects in the organisms and molecules on exposure to UV radiations. The presence of effective ozone gas layer in the stratosphere allows light only with the wavelength greater than 290 nm to reaches the earth surface.\(^1\) At the earth’s surface, sunlight is composed of about 7% UV, 44% visible and 49% other radiations (Figure 2.1). Although only a relatively small amount of the sunlight energy is in the UV region of 290-400, it is ample to induce photochemical reaction/degradation of many organic molecules.\(^1\)

![Solar radiation spectrum](image)

**Figure 2.1.** Solar radiation spectrum\(^1\)

The damaging UV radiation in the sunlight is responsible for the discoloration of dyes and pigments, weathering and yellowing of plastics, loss of gloss and
mechanical properties (cracking), sunburnt skin, degradation of pesticides/bi-pesticides and other problems associated to UV light.

A long standing problem in agricultural field is menace of various pests damaging the useful crops. The use of insecticides in agriculture is continuously increasing with simultaneous addition of new types of insecticides. The development of effective insecticides has obviously been a major activity in the past decades for controlling the ruinous attack by the pests. A wide range of insecticides including organophosphorus, carbamates, pyrethroids and other class of pesticides have been used on crops to control insects.

There are many factors which affect the insecticidal activity when exposed to external environment like microbial decomposition, hydrolysis, volatilization and photolysis. Photodegradation due to sunlight is one of the major pathways which lessen insecticidal activity after their application in the field. On exposure to sunlight, the insecticide molecules undergo a variety of primary processes often leading to their degradation (Figure 2.2).¹ ²

![Diagram of insecticides degradation processes](image)

**Figure 2.2.** Various primary processes of insecticides on exposure to UV light
To overcome these problem chemical modifications were attempted\(^3\) which seriously affected the insecticidal activity and also caused ecological problems.\(^4\) Alternatively, the UV absorbing molecules, also known as photostabilizers were used in the formulations to extend the environmental life of the insecticides.\(^5\)-\(^8\)

Chlorpyrifos 1, \(O,O\)-diethyl \(O\)-(3,5,6-trichloro-2-pyridyl) phosphorothioate (\(\text{C}_9\text{H}_{11}\text{Cl}_3\text{NO}_3\text{PS}\)), is most widely used insecticide all over the world for the protection against variety of pests. It is used both for agriculture and household purposes. US alone uses almost 30 million pounds per year\(^9\) while in Europe, more than 50,000 kg/year are used.\(^10\) It is used for various crops such as corn, alfalfa, cotton, soybeans, cereals, tobacco, peaches, vegetables and citrus fruits to control a wide spectrum of chewing, sucking and boring insects like aphids, caterpillars, Helicoverpa spp, mites, moths, jassids, budworm, stem borer and locusts.

\begin{center}
\begin{tikzpicture}

\node at (0,0) {\text{Cl}};
\node at (1,0) {\text{Cl}};
\node at (0.5,0.5) {\text{N}};
\node at (0.5,-0.5) {\text{S}};
\node at (0,-0.5) {\text{Cl}};
\node at (1,-0.5) {\text{Cl}};
\node at (0.5,1.5) {\text{S}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{P}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{C}_2\text{H}_5};
\node at (1,0.5) {\text{C}_2\text{H}_5};
\node at (0.5,-0.5) {\text{C}_2\text{H}_5};
\node at (1,-0.5) {\text{C}_2\text{H}_5};
\node at (0.5,1.5) {\text{C}_2\text{H}_5};
\end{tikzpicture}
\end{center}

Chlorpyrifos 1

\begin{center}
\begin{tikzpicture}

\node at (0,0) {\text{C}_2\text{H}_5};
\node at (0,-0.5) {\text{C}_2\text{H}_5};
\node at (0,0) {\text{S}};
\node at (0,-0.5) {\text{P}};
\node at (0,-0.5) {\text{O}};
\node at (0,-0.5) {\text{O}};
\node at (0,-0.5) {\text{C}_2\text{H}_5};
\node at (0,0) {\text{Cl}};
\node at (0,-0.5) {\text{Cl}};
\node at (0,0) {\text{C}_2\text{H}_5};
\end{tikzpicture}
\end{center}

Sulfotep 2

\begin{center}
\begin{tikzpicture}

\node at (0,0) {\text{Cl}};
\node at (1,0) {\text{Cl}};
\node at (0.5,0.5) {\text{N}};
\node at (0.5,-0.5) {\text{S}};
\node at (0,-0.5) {\text{Cl}};
\node at (1,-0.5) {\text{Cl}};
\node at (0.5,1.5) {\text{S}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{P}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{O}};
\node at (0.5,0.5) {\text{C}_2\text{H}_5};
\node at (1,0.5) {\text{C}_2\text{H}_5};
\node at (0.5,-0.5) {\text{C}_2\text{H}_5};
\end{tikzpicture}
\end{center}

Chlorpyrifos-oxon 3

\begin{center}
Scheme 2.1. Photodegradation of chlorpyrifos to chlorpyrifos-oxon and sulfotep
\end{center}
Chlorpyrifos is also subject to degradation on exposure to sunlight resulting in formation of various photoproducts which are more stable to UV radiation than chlorpyrifos itself. Chlorpyrifos-oxon 3 is one such photoproduct which is more persistent and about 3000 times more toxic to humans than chlorpyrifos (Scheme 2.1).\textsuperscript{11-13} On exposure to UV light, sulfotep 2 is also formed from chlorpyrifos (Scheme 2.1) which is highly toxic and often exists as an impurity in chlorpyrifos.\textsuperscript{14}

In order to extend environmental life of chlorpyrifos and consequently to minimize the formation of toxic, UV stable photoproducts, use of effective and efficient photostabilizers is indispensable. The photostabilizers absorb UV radiation and dissipate the absorbed energy harmlessly and also persist in the matrix for the expected lifetime. Photostabilization of the insecticide can take place either by preferential absorption of light by photostabilizer, thereby preventing photo-excitation of the insecticide molecules or transfer of excess energy from the excited insecticide molecules to the photostabilizers through various energy transfer mechanisms such as excited-state intramolecular proton transfer (ESIPT) or keto-enol tautomerism.\textsuperscript{15,16}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure2.3.png}
\caption{Intramolecularly H-bonded photostabilizers}
\end{figure}
Intramolecularly H-bonded photostabilizers such as hydroxyphenyl-benzotriazoles 4, hydroxyphenyl-s-triazines 5, oxanilides 6 and 2-hydroxybenzophenones 7 are widely used for the protection of various products against photodegradation (Figure 2.3).\textsuperscript{17-19}

\begin{center}
\includegraphics[width=\textwidth]{Scheme2.2.png}
\end{center}

**Scheme 2.2.** Photo-Fries type rearrangement of phenyl salicylate under UV light

Earlier our group has studied the effect of photostabilization of azadirachtin-A on exposure to UV light in the presence of four structurally different photostabilizers, namely 4-aminobenzoic acid, 2,4-dihydroxybenzophenone, 4,4’-dihydroxybenzophenone and phenyl salicylate.\textsuperscript{20, 21} It was found that among all the photostabilizers studied, only phenyl salicylate provided the best photostabilization. It was proposed that on exposure to UV light, phenyl salicylate 8 does not dissipate absorbed energy by direct absorption of UV light but instead undergoes Photo-Fries type rearrangement to form strongly absorbing 2,2’- and 2,4’-dihydroxy benzophenones (Scheme 2.2). These two molecules then dissipate absorbed energy through ESIPT.

2-Hydroxybenzophenones are known to act as photostabilizer via ESIPT involving dissipation of absorbed light energy through nonphotochemical pathways.\textsuperscript{22-26} These compounds possess an efficient radiationless mechanism (keto-enol tautomerism) of energy dissipation. The molecule in the first excited state PS\textsubscript{1} undergoes ESIPT to generate another species in its first excited singlet state PS\textsubscript{2}. This excited proton-transferred species loses its energy by a nonradiative decay process to form PS\textsubscript{3}. It should be noted that the contribution of this energy towards thermal degradation of the compound is negligible compared to the much stronger thermal energy reaching the compound from the solar radiation.\textsuperscript{22} The original form of the
**Scheme 2.3.** Excited State Intramolecular Proton Transfer (ESIPT) of o-hydroxy benzophenones

photostabilizer PS₀ is regenerated by a reverse proton transfer mechanism. In 2-hydroxybenzophenone, it is the proximity of hydroxyl and keto groups in the molecule which is thought to be responsible for such photostabilization.

In continuation with our research directed towards design and synthesis of novel photostabilizers, we conceived benzils having structures of the type 3 (Scheme 2.4) with two such hydroxy and keto pairs assembled into a single structure. It was envisioned that these benzils would possess enhanced efficiency and usefulness as photostabilizers due to the inherent structural features.
2.3 Results and discussion

To ascertain our contemplation, novel 2,2’-dihydroxy-4,4’-dialkoxy benzils 13(a-h) were synthesized from various 1,4-dialkoxy benzenes 12(a-h) (Scheme 2.4) by an intermolecular Friedel-Crafts acylation with oxalyl chloride, using CS$_2$ as solvent.$^{27}$

\[
\begin{align*}
\text{OH} & \quad \text{RBr, K$_2$CO$_3$, Acetone, Reflux, 9 hrs} & \quad \text{OR} \\
\text{11} & \quad \text{12(a-h)} \\
\text{12(a-h)} & \quad \text{Oxalyl Chloride, Anhydrous AlCl$_3$, CS$_2$, 0$^\circ$C to rt} & \quad \text{13(a-h)} \\
\end{align*}
\]

\[
\begin{align*}
a & : \text{R= CH}_3; \\ b & : \text{R= C}_2\text{H}_5; \\ c & : \text{R= n-C}_3\text{H}_7; \\ d & : \text{n-C}_4\text{H}_9; \\ e & : \text{R= n-C}_6\text{H}_{13}; \\ f & : \text{R= n-C}_8\text{H}_{17}; \\ g & : \text{R= n-C}_{10}\text{H}_{21}; \\ h & : \text{R= n-C}_{12}\text{H}_{25} \\
\end{align*}
\]

**Scheme 2.4.** Synthesis of novel benzil derivatives

The structures of compounds 13(a-h) were confirmed by FTIR, $^1$H NMR, $^{13}$C NMR, mass and elemental analysis. The FTIR spectrum of 13g showed bands at 1471, 1600 cm$^{-1}$ for aromatic ring and a strong band at 1633 cm$^{-1}$ for the carbonyl group. The $^1$H NMR spectrum of 13g displayed a singlet at $\delta$ 0.89 for two methyl protons and multiplets at $\delta$ 1.34, 1.45, 1.80 for 32 methylene protons of alkyl chain. The triplet at $\delta$ 4.0 showed the presence of 4 methylene protons attached to oxygen and a singlet at $\delta$ 11.86 for two protons of hydroxyl group. The $^{13}$C NMR spectrum of 13g exhibited signal at $\delta$ 14.14 for carbon of methyl group, signals at $\delta$ 22.69, 25.89,
28.85, 29.30, 29.31, 29.54, 31.89, 68.77 for methylene carbon of alkyl chain, signals at δ 101.58, 109.35, 110.79, 134.00, 166.76, 167.38 for aromatic carbons along with signal at δ 194.45 for carbonyl carbon. The structure of 13g was further confirmed by its mass spectrum which gave a molecular ion peak at 554. The elemental analysis was in good agreement with the required for C_{34}H_{50}O_{6} and it was found: C, 73.4; H, 9.2 and calculated: C, 73.6; H, 9.1.

The FTIR spectrum of 13h showed bands at 1471, 1581 cm\(^{-1}\) for aromatic ring and a strong band at 1635 cm\(^{-1}\) for the carbonyl group. The \(^1\)H NMR spectrum of 13h displayed a singlet at δ 0.80 for two methyl protons and multiplets at δ 1.21, 1.35, 1.71 for 40 methylene protons of alkyl chain. The triplet at δ 3.9 showed the presence of 4 methylene protons attached to oxygen and a singlet at δ 11.77 for two protons of hydroxyl group. The \(^{13}\)C NMR spectrum of 13h exhibited signal at δ 14.13 for carbon of methyl group, signals at δ 22.69, 25.89, 28.85, 29.29, 29.35, 29.52, 29.57, 29.63, 29.64, 31.92, 68.77 for methylene carbon of alkyl chain, signals at δ 101.58, 109.34, 110.80, 134.00, 166.76, 167.38 for aromatic carbons along with signal at δ 194.45 for carbonyl carbon. The structure of 13h was further confirmed by its mass spectrum which gave a molecular ion peak at 610. The elemental analysis was in good agreement with the required for C_{38}H_{58}O_{6} and it was found: C, 74.6; H, 9.7 and calculated: C, 74.7; H, 9.6.

The novel benzils 13(a-h) are then subjected to photostabilization study. The photostability of chlorpyrifos in the presence of benzils 13(a-h) was compared with that using the reference photostabilizer i.e. 2,4-dihydroxybenzophenone. The standard solutions of pure chlorpyrifos with (1:1) and without (1:0) benzil photostabilizers were irradiated in a Pyrex immersion–well type photochemical reactor (Figure 2.4) using a high-pressure mercury vapor lamp (MPMV, 250W, Bajaj, India). After 10h, the irradiated solutions were analyzed for their chlorpyrifos content by analytical HPLC. The percentage remaining of chlorpyrifos recovered from the solutions after 10 hours of exposure to UV radiation are shown in Table 1.
Figure 2.4. Immersion-well type photo reactor

Figure 2.5. HPLC chromatogram of pure chlorpyrifos
Figure 2.6. HPLC chromatogram of pure chlorpyrifos (no photostabilizer) after 10h irradiation under UV light

Figure 2.7. HPLC chromatogram of chlorpyrifos (1 chlorpyrifos : 1 photostabilizer 13h) after 10h irradiation under UV light
Figure 2.5, 2.6 and 2.7 shows HPLC chromatogram of pure chlorpyrifos, pure chlorpyrifos (no UV absorber) and pure chlorpyrifos (1 chlorpyrifos : 1 UV absorber 13h) following ten hours of exposure of UV light, respectively.

In case of pure chlorpyrifos (no photostabilizer) following ten hours of exposure to UV radiation, HPLC chromatogram showed reduction of the peak height at 3.733 (tr) corresponding to pure chlorpyrifos and appearance of a number of unidentified peaks (Figure 2.6).

The recovery of chlorpyrifos was found to be only 66.12 % in the absence of photostabilizers when exposed to UV light while that in the presence of known photostabilizer, 2,4-dihydroxybenzophenone was 78.80 %. Thus the photostabilization of chlorpyrifos induced by 2,4-dihydroxybenzophenone was found to be upto 12.68 %. We further found that benzil derivatives (13a-h), provided photostabilizing effect up to 30.51 % i.e. up to 96.63 % of chlorpyrifos was recovered after irradiation experiments as compared to UV exposure of bare chlorpyrifos. (Table 2.1)

**Table 2.1.** Percentage recovery of Chlorpyrifos in presence and absence of photostabilizer on exposure to UV radiation

(Chlorpyrifos: UV absorber, 1:1 mole ratio)

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Samples</th>
<th>% recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Chlorpyrifos (no stabilizer )</td>
<td>66.12</td>
</tr>
<tr>
<td>2</td>
<td>2,4-dihydroxy benzophenone C_{13}H_{10}O_{3}</td>
<td>78.80</td>
</tr>
<tr>
<td>3</td>
<td>C_{16}H_{14}O_{6} (13a)</td>
<td>89.83</td>
</tr>
<tr>
<td>4</td>
<td>C_{18}H_{18}O_{6} (13b)</td>
<td>89.00</td>
</tr>
<tr>
<td>5</td>
<td>C_{20}H_{22}O_{6} (13c)</td>
<td>95.53</td>
</tr>
<tr>
<td>6</td>
<td>C_{22}H_{26}O_{6} (13d)</td>
<td>94.42</td>
</tr>
<tr>
<td>7</td>
<td>C_{26}H_{34}O_{6} (13e)</td>
<td>96.44</td>
</tr>
<tr>
<td>8</td>
<td>C_{30}H_{42}O_{6} (13f)</td>
<td>96.62</td>
</tr>
<tr>
<td>9</td>
<td>C_{34}H_{50}O_{6} (13g)</td>
<td>89.90</td>
</tr>
<tr>
<td>10</td>
<td>C_{38}H_{58}O_{6} (13h)</td>
<td>96.63</td>
</tr>
</tbody>
</table>
Absorption spectra of chlorpyrifos and photostabilizers

Figure 2.8. UV spectrum of chlorpyrifos

Figure 2.8 and 2.9 show the absorption spectra of pure chlorpyrifos, 2,4-dihydroxybenzophenone and benzil (13a) photostabilizers in methanol. The UV spectra of pure chlorpyrifos and benzils show that both of them absorb strongly near 289 nm and 287 nm respectively. Effective photostabilization of chlorpyrifos by benzil photostabilizers appears to be due to competitive energy absorption of UV photons which cause degradation of chlorpyrifos.

Figure 2.9. UV spectra of benzil and 2,4-dihydroxybenzophenone
The UV spectra of 2,4-dihydroxybenzophenone and benzil photostabilizers are almost identical and absorb strongly near 287 nm (Figure 2.9). Less recovery of chlorpyrifos was observed in case of 2,4-dihydroxybenzophenone which has one hydroxy-keto pair that can photostabilize chlorpyrifos through ESIPT. However in case of benzil derivatives there are two such hydroxy-keto pairs which are perhaps responsible for more efficient photostabilization of chlorpyrifos. The use of such photostabilizers in the formulations of expensive pesticides might reduce use of their excessive quantities during actual field application on larger scale thereby adding attractive economical and environmental benefits.

2.4 Experimental

Chemicals

Chlorpyrifos (99 %) was gifted by the United Phosphorus Limited (India) while the rest of the chemicals and HPLC solvents were purchased from Glaxo (Qualigens) India Ltd.

HPLC Instrumentation

The HPLC used in the study was Shimadzu LC 20AT equipped with a variable wavelength detector (SPD 20A), flow controller and Class-VP software. The instrument employed dual solvent system and dual pump heads with common drive which gave sable and reproducible flows. The Class-VP provided the chromatogram, percent area and retention time ($t_{R}$) for each peak.

Standard Solutions

Standard solutions of pure chlorpyrifos (0.5 mg/mL) were prepared along with photostabilizers in the mole ratio of 1:1 (Chlorpyrifos : Photostabilizer) and 1:0 (no
photostabilizer) in dry methanol. The solutions were stored in amber colored bottles between 0-4°C and the chlorpyrifos content was determined by analytical HPLC.

**Irradiation Experiments**

The standard solutions of pure chlorpyrifos prepared as above with and without photostabilizers in methanol (20 ml) were placed in a Pyrex immersion–well type photochemical reactor and irradiated separately using a high-pressure mercury vapor lamp (HPMV, 250 W, Bajaj India) at a distance of 3.8 cm from the source. The solutions were withdrawn after irradiation for 10h and analyzed for the chlorpyrifos content by analytical HPLC. Control samples were irradiated and analyzed similarly.

**General**

UV spectra were recorded on a Shimadzu UV-2450 UV/Visible Spectrophotometer. FTIR spectra were recorded on a Shimadzu 8400S FTIR spectrometer using KBr. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker-400MHz NMR spectrometer (100 MHz for $^{13}$C NMR) using CDCl$_3$ or DMSO-$d_6$ (TMS as an internal standard). Mass spectra were obtained on a Shimadzu QP-5050 mass spectrometer. Column chromatography was carried out on Acme’s silica gel (60-120 mesh size) and eluted using mixtures of light petroleum and ethyl acetate. Thin layer chromatography was performed using Acme’s silica gel for TLC and spots were visualized in the iodine vapor. Percentage yields were reported based upon the recovery of starting materials. The structures of all the compounds were confirmed by their mp, elemental analysis, FTIR, $^1$H NMR, $^{13}$C NMR and mass spectrometric data.

Identification and quantitative analysis of chlorpyrifos in the sample solution was done using methanol as mobile phase by high performance liquid chromatography (HPLC) equipped with a SPD 20A variable wavelength UV-Vis detector. The HPLC column was fitted with a 4.6 mm ID, 250 mm length, Hypersil ODS and 5 micron particle size.
**General procedure for the synthesis of Dialkoxy benzenes:**

A mixture of 45 mmol of 1,3-dihydroxy benzene 1, 108 mmol of appropriate alkyl bromide and 135 mmol of powdered potassium carbonate was stirred in dry acetone (50ml) for 9h under reflux. After completion of the reaction (TLC), the reaction mixture was allowed to cool to room temperature, filtered through a celite pad and acetone was distilled off. Water was added to the residue and the aqueous layer was extracted with ethyl acetate (4x25 ml) and the combined organic layers were washed with water (2x20 ml), brine (2x20 ml), dried over anhydrous sodium sulphate. The solvent was removed on rotavapor and the resulting residue was chromatographed over silica gel using a mixture of light petroleum and ethyl acetate as eluents.

**1,3-Diethoxybenzene (12b)**

Colourless liquid, $\lambda_{\text{max}}$ (EtOAc)/nm: 270; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2980 (CH), 1047 (C-O); $^1$H NMR (400MHz, CDCl$_3$): $\delta_H$ 1.44 (t, 6H, $J$ = 7.2 Hz, CH$_3$), 4.04 (q, 4H, CH$_2$), 6.51 (m, 3H, Ar), 7.19 (t, 1H, $J$ = 8.4 Hz, Ar).

**1,3-Di-n-propoxybenzene (12c)**

Colourless liquid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2964 (CH), 1012 (C-O); $^1$H NMR (400MHz, CDCl$_3$): $\delta_H$ 1.07 (t, 6H, $J$ = 7.2 Hz, CH$_3$), 1.84 (m, 4H, CH$_2$), 3.93 (t, 4H, $J$ = 6.8 Hz, O-CH$_2$), 6.52 (m, 3H, Ar), 7.19 (t, 1H, $J$ = 8.4 Hz, Ar).

**1,3-Di-n-butoxybenzene (12d)**

Colourless liquid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2968 (CH), 1031 (C-O); $^1$H NMR (400MHz, CDCl$_3$): $\delta_H$ 1.04 (t, 6H, $J$ = 7.6 Hz, CH$_3$), 1.55 (m, 4H, CH$_2$), 1.82 (m, 4H, CH$_2$), 4.0 (t, 4H, $J$ = 6.8 Hz, O-CH$_2$), 6.55 (m, 3H, Ar), 7.20 (t, 1H, $J$ = 8.4 Hz, Ar).

**1,3-Bis-n-(hexyloxy)benzene (12e)**

Colourless liquid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2965 (CH), 1045 (C-O); $^1$H NMR (400MHz, CDCl$_3$): $\delta_H$ 0.96 (t, 6H, $J$ = 7.2 Hz, CH$_3$), 1.36 (m, 8H, CH$_2$), 1.50 (m, 4H, CH$_2$), 1.81 (m, 4H, CH$_2$), 3.96 (t, 4H, $J$ = 6.8 Hz, O-CH$_2$), 6.52 (m, 3H, Ar), 7.20 (t, 1H, $J$ = 8.0 Hz, Ar).
1,3-Bis-n-(octyloxy)benzene (12f)

White crystalline solid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2953 (CH), 1043 (C=O); $^1$H NMR (400MHz, CDCl$_3$): $\delta$H 0.99 (t, 6H, $J = 7.2$ Hz, CH$_3$), 1.35 (m, 16H, CH$_2$), 1.45 (m, 4H, CH$_2$), 1.78 (m, 4H, CH$_2$), 3.94 (t, 4H, $J = 6.4$ Hz, O-CH$_2$), 6.49 (m, 3H, Ar), 7.20 (t, 1H, $J = 8.0$ Hz, Ar); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$C 14.14 (CH$_3$), 22.69, 26.08, 29.27, 29.28, 29.39, 31.84 (CH$_2$), 67.97 (O-CH$_2$), 101.36, 106.59, 129.75 (Ar), 160.37 (C-OR).

1,3-Bis-n-(decyloxy)benzene (12g)

White crystalline solid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2961 (CH), 1022 (C=O); $^1$H NMR (400MHz, CDCl$_3$): $\delta$H 0.90 (t, 6H, $J = 7.2$ Hz, CH$_3$), 1.35 (m, 24H, CH$_2$), 1.45 (m, 4H, CH$_2$), 1.75 (m, 4H, CH$_2$), 3.94 (t, 4H, $J = 6.8$ Hz, O-CH$_2$), 6.49 (m, 3H, Ar), 7.17 (t, 1H, $J = 8.4$ Hz, Ar).

1,3-Bis-n-(dodecyloxy)benzene (12h)

White crystalline solid, $\lambda_{\text{max}}$ (EtOAc)/nm: 274; IR ($\nu_{\text{max}}$, cm$^{-1}$): 2955 (CH), 1045 (C=O); $^1$H NMR (400MHz, CDCl$_3$): $\delta$H 0.90 (t, 6H, $J = 7.2$ Hz, CH$_3$), 1.29 (m, 32H, CH$_2$), 1.46 (m, 4H, CH$_2$), 1.78 (m, 4H, CH$_2$), 3.94 (t, 4H, $J = 6.8$ Hz, O-CH$_2$), 6.49 (m, 3H, Ar), 7.17 (t, 1H, $J = 8.4$ Hz, Ar); $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$C 14.17 (CH$_3$), 22.74, 26.09, 29.31, 29.40, 29.45, 29.63, 29.65, 29.69, 29.71, 31.97 (CH$_2$), 67.95 (O-CH$_2$), 101.35, 106.58, 129.75 (Ar), 160.37 (C-OR).

General procedure for the synthesis of Dialkoxy Benzils:

To a mechanically stirred suspension of 7.2 mmol of dialkoxy benzene and 7.9 mmol of anhydrous aluminium chloride in carbon disulfide (100 ml) at 0°C was added a solution of 4.7 mmol of oxalyl chloride in carbon disulfide (50 ml) over a period of 4 h under a constant stream of nitrogen. Stirring was continued for 18 h after which the resulting mixture was poured onto ice and carbon disulfide was distilled off. The aqueous mixture was extracted with ethyl acetate (4x25 ml) and the combined organic layers were washed with water (2x20 ml), brine (2x20 ml), dried over anhydrous sodium sulphate. The solvent was removed on rotavapor and the resulting residue was chromatographed over silica gel using a mixture of light petroleum and ethyl acetate as eluents.
1,2-Bis(2-hydroxy-4-methoxyphenyl)ethane-1,2-dione (13a)

White crystalline solid; mp 150°C; \( \lambda_{\text{max}} \) (EtOAc)/nm: 284; IR (\( v_{\text{max}} \), cm\(^{-1} \)): 1024 (C-O), 1629 (C=O), 3076 (CH); \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta_H \) 3.89 (s, 6H, O-CH\(_3\)), 6.45 (dd, 2H, \( J_1 = 2.4 \text{ Hz}, J_2 = 2.4 \text{ Hz}, \text{Ar} \)), 6.52 (d, 2H, \( J = 2.4 \text{ Hz}, \text{Ar} \)), 7.42 (d, 2H, \( J = 8.8 \text{ Hz}, \text{Ar} \)), 11.86 (s, 2H, OH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \( \delta_C \) 55.86 (O-CH\(_3\)), 101.17, 109.03, 110.95, 134.04, 166.80 (C-OH), 167.76 (C-OR), 194.47 (Keto carbon); MS: m/z 301.13(M\(^+\)). Anal. Calc. for C\(_{18}\)H\(_{14}\)O\(_6\): C, 63.6; H, 4.7. Found: C, 63.4; H, 4.8.

1,2-Bis(4-ethoxy-2-hydroxyphenyl)ethane-1,2-dione (13b)

White crystalline solid; mp 130°C; \( \lambda_{\text{max}} \) (EtOAc)/nm: 287; IR (\( v_{\text{max}} \), cm\(^{-1} \)): 1043 (C-O), 1633 (C=O), 2983 (CH); \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta_H \) 1.43 (t, 6H, \( J = 7.2 \text{ Hz}, \text{CH}_3 \)), 4.14 (q, 4H, O-CH\(_2\)), 6.42 (dd, 2H, \( J_1 = 2.4 \text{ Hz}, J_2 = 2.4 \text{ Hz}, \text{Ar} \)), 6.49 (d, 2H, \( J = 2.4 \text{ Hz}, \text{Ar} \)), 7.42 (d, 2H, \( J = 8.8 \text{ Hz}, \text{Ar} \)), 11.86 (s, 2H, -OH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \( \delta_C \) 14.49 (CH\(_3\)), 64.33 (O-CH\(_2\)), 101.55, 109.33, 110.81, 134.04, 166.76 (C-OH), 167.18 (C-OR), 194.45 (Keto carbon); MS: m/z 330.22 (M\(^+\)). Anal. Calc. for C\(_{18}\)H\(_{14}\)O\(_6\): C, 65.4; H, 5.5. Found: C, 65.3; H, 5.5.

1,2-Bis(2-hydroxy-4-n-propoxyphenyl)ethane-1,2-dione (13c)

White crystalline solid, mp 117°C; \( \lambda_{\text{max}} \) (EtOAc)/nm: 285; IR (\( v_{\text{max}} \), cm\(^{-1} \)): 1018 (C-O), 1622 (C=O), 2966 (CH); \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta_H \) 0.89 (t, 6H, \( J = 6.8 \text{ Hz}, \text{CH}_3 \)), 1.80 (m, 4H, CH\(_2\)), 4.04 (t, 4H, \( J = 6.8 \text{ Hz}, \text{O-CH}_2 \)), 6.44 (dd, 2H, \( J_1 = 2.4 \text{ Hz}, J_2 = 2.4 \text{ Hz}, \text{Ar} \)), 6.49 (d, 2H, \( J = 2.4 \text{ Hz}, \text{Ar} \)), 7.40 (d, 2H, \( J = 8.8 \text{ Hz}, \text{Ar} \)), 11.86 (s, 2H, OH); \(^{13}\)C NMR (100MHz, CDCl\(_3\)): \( \delta_C \) 14.14 (CH\(_3\)), 22.69 (CH\(_2\)), 68.77 (O-CH\(_2\)), 101.57, 109.35, 110.79, 134.00, 166.76 (C-OH), 167.38 (C-OR), 194.45 (Keto carbon); MS: m/z 358.11 (M\(^+\)). Anal. Calc. for C\(_{20}\)H\(_{22}\)O\(_6\): C, 67.0; H, 6.2. Found: C, 67.1; H, 6.3.

1,2-Bis(4-n-butoxy-2-hydroxyphenyl)ethane-1,2-dione (13d)

White crystalline solid, mp 107°C; \( \lambda_{\text{max}} \) (EtOAc)/nm: 287; IR (\( v_{\text{max}} \), cm\(^{-1} \)): 1058 (C-O), 1630 (C=O), 2962 (CH); \(^1\)H NMR (400MHz, CDCl\(_3\)): \( \delta_H \) 1.49 (t, 6H, \( J = 7.2 \text{ Hz}, \text{CH}_3 \)), 1.52 (m, 4H, CH\(_2\)), 1.80 (m, 4H, CH\(_2\)), 4.04 (t, 4H, \( J = 6.8 \text{ Hz}, \text{O-CH}_2 \)), 6.44
(dd, 2H, J₁ = 2.4 Hz, J₂ = 2.4 Hz, Ar), 6.49 (d, 2H, J = 2.0 Hz, Ar), 7.40 (d, 2H, J = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ¹³C NMR (100MHz, CDCl₃): δ_C 13.77 (CH₃), 19.12, 30.86 (CH₂), 68.45 (O-CH₂), 101.55, 109.37, 110.78, 134.01, 166.76 (C-OH), 167.39 (C-OR), 194.46 (Keto carbon); MS: m/z 385.88 (M⁺). Anal. Calc. for C₂₂H₂₆O₆: C, 68.4; H, 6.8. Found: C, 68.6; H, 6.7.

1,2-Bis(4-n-hexyloxy-2-hydroxyphenyl)ethane-1,2-dione (13e)

White crystalline solid, mp 94°C; λ_max (EtOAc)/nm: 287; IR (v_max, cm⁻¹): 1022 (C-O), 1633 (C=O), 2964 (CH); ¹H NMR (400MHz, CDCl₃): δ_H 0.93 (t, 6H, J = 6.8 Hz, CH₃), 1.34 (m, 8H, CH₂), 1.46 (m, 4H, CH₂), 1.80 (m, 4H, CH₂) 4.03 (t, 4H, J = 6.8 Hz, O-CH₂), 6.44 (dd, 2H, J₁ = 2.4 Hz, J₂ = 2.4 Hz, Ar), 6.49 (d, 2H, J = 2.4 Hz, Ar), 7.40 (d, 2H, J = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ¹³C NMR (100 MHz, CDCl₃): δ_C 14.04 (CH₃), 22.57, 25.57, 28.82, 31.47 (CH₂), 68.76 (O-CH₂), 101.56, 109.35, 110.78, 134.01, 166.76 (C-OH), 167.38 (C-OR), 194.45 (Keto carbon); MS: m/z 441.93 (M⁺). Anal. Calc. for C₃₆H₃₄O₆: C, 70.6; H, 7.7. Found: C, 70.7; H, 7.6.

1,2-Bis(2-hydroxy-4-n-octyloxyphenyl)ethane-1,2-dione (13f)

White crystalline solid, mp 98°C; λ_max (EtOAc)/nm: 287; IR (v_max, cm⁻¹): 1030 (C-O), 1620 (C=O), 2945 (CH); ¹H NMR (400MHz, CDCl₃): δ_H 0.91 (t, 6H, J = 6.8 Hz, CH₃), 1.34 (m, 16H, CH₂), 1.46 (m, 4H, CH₂), 1.80 (m, 4H, CH₂) 4.03 (t, 4H, J = 6.8 Hz, O-CH₂), 6.44 (dd, 2H, J₁ = 2.4 Hz, J₂ = 2.4 Hz, Ar), 6.49 (d, 2H, J = 2.4 Hz, Ar), 7.40 (d, 2H, J = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ¹³C NMR (100 MHz, CDCl₃): δ_C 14.12 (CH₃), 22.66, 25.90, 28.85, 29.20, 29.26, 31.79 (CH₂), 68.77 (O-CH₂), 101.56, 109.36, 110.78, 134.04, 166.76 (C-OH), 167.38 (C-OR), 194.45 (Keto carbon); MS: m/z 497.84 (M⁺). Anal. Calc. for C₃₆H₄₂O₆: C, 72.2; H, 8.5. Found: C, 72.3; H, 8.3.

1,2-Bis(4-n-decyloxy-2-hydroxyphenyl)ethane-1,2-dione (13g)

White crystalline solid, mp 105°C; λ_max (EtOAc)/nm: 287; IR (v_max, cm⁻¹): 1018 (C-O), 1633 (C=O), 3082 (CH); ¹H NMR (400MHz, CDCl₃): δ_H 0.89 (t, 6H, J = 6.8 Hz, CH₃), 1.34 (m, 24H, CH₂), 1.45 (m, 4H, CH₂), 1.80 (m, 4H, CH₂), 4.0 (t, 4H, J = 6.8 Hz, O-CH₂), 6.44 (dd, 2H, J₁ = 2.4 Hz, J₂ = 2.4 Hz, Ar), 6.49 (d, 2H, J = 2.4 Hz, Ar), 7.40 (d, 2H, J = 8.8 Hz, Ar), 11.86 (s, 2H, OH); ¹³C NMR (100 MHz, CDCl₃): δ_C 14.14 (CH₃), 22.69, 25.89, 28.85, 29.30, 29.31, 29.54, 31.89, 68.77 (O-CH₂), 101.58,
109.35, 110.79, 134.00, 166.76 (C-OH), 167.38 (C-OR), 194.45 (Keto carbon); MS: m/z 553.99 (M⁺). Anal. Calc. for C₃₄H₅₀O₆: C, 73.6; H, 9.1. Found: C, 73.4; H, 9.2.

**1,2-Bis(4-n-dodecyloxy-2-hydroxyphenyl)ethane-1,2-dione (13h)**

White crystalline solid, mp 90°C; λ_max (EtOAc)/nm: 285; IR (ν_max, cm⁻¹): 1026 (C-O), 1635 (C=O), 2955 (CH); ¹H NMR (400MHz, CDCl₃): δ_H 0.80 (t, J = 6.8 Hz, 6H, CH₃), 1.21 (m, 32H, CH₂), 1.35 (m, 4H, CH₂), 1.71 (m, 4H,CH₂), 3.9 (t, J = 6.8 Hz, 4H, O-CH₂), 6.35 (dd, 2H, J₁ = 2.4 Hz, J₂ = 2.4 Hz, Ar), 6.40 (d, 2H, J = 2.4 Hz, Ar), 7.31 (d, 2H, J = 8.8 Hz, Ar), 11.77 (s, 2H, OH); ¹³C NMR (100 MHz, CDCl₃): δ_C 14.13 (CH₃), 22.69, 25.89, 28.85, 29.29, 29.35, 29.52, 29.57, 29.63, 29.64, 31.92, 68.77 (O-CH₂), 101.58, 109.34, 110.80, 134.00, 166.76 (C-OH), 167.38 (C-OR), 194.45 (Keto carbon); MS: m/z 610.63 (M⁺). Anal. Calc. for C₃₈H₅₈O₆: C, 74.7; H, 9.6. Found: C, 74.6; H, 9.7.

**2.5 Conclusion**

Synthesis and application of novel benzil derivatives as photostabilizers is reported. A systematic photostabilization study of known and widely used insecticide, chlorpyrifos was carried out using novel benzils under UV light. The percentage recovery of chlorpyrifos showed a significant enhancement in photostabilization of chlorpyrifos by benzil derivatives as compared to 2,4-dihydroxybenzophenone as a reference. Thus it is possible to minimize generation of toxic impurities resulting from photochemical decomposition of chlorpyrifos in field by employing suitable photostabilizers such as benzil derivatives presented in this chapter.
2.6 Spectra
Figure 2.10: $^1$H NMR of 1,3-diethoxybenzene (12b)
Figure 2.11: $^1$H NMR of 1,3-di-n-propanoxybenzene (12c)
Figure 2.12: $^1$H NMR of 1,3-di-n-butoxybenzene (12d)
Figure 2.13: $^1$H NMR of 1,3-bis-n-(hexyloxy)benzene (12e)
Figure 2.14: $^1$H NMR of 1,3-bis-n-(octyloxy)benzene (12f)
Figure 2.15: $^{13}$C NMR of 1,3-bis-octyloxy)benzene (12f).
Figure 2.16: $^1$H NMR of 1,3-bis-n-(decoxy)benzene (12g)
Figure 2.17: $^1$H NMR of 1,3-bis-n-(dodecyloxy)benzene (12h)
Figure 2.18: $^{13}$C NMR of 1,3-bis-n-(dodecyloxy)benzene (12h)
Figure 2.19: $^1$H NMR of 1,2-bis(2-hydroxy-4-methoxyphenyl)ethane-1,2-dione (13a)
Figure 2.20: $^{13}$C NMR of 1,2-bis(2-hydroxy-4-methoxyphenyl)ethane-1,2-dione (13a)
Figure 2.21: Mass Spectrum 1,2-bis(2-hydroxy-4-methoxyphenyl)ethane-1,2-dione (13a)
Figure 2.22: $^1$H NMR of 1,2-bis(4-ethoxy-2-hydroxyphenyl)ethane-1,2-dione (13b)
Figure 2.23: $^{13}$C NMR of 1,2-bis(4-ethoxy-2-hydroxyphenyl)ethane-1,2-dione (13b)
Figure 2.24: Mass Spectrum of 1,2-bis(4-ethoxy-2-hydroxyphenyl)ethane-1,2-dione (13b)
Figure 2.25: $^1$H NMR of 1,2-bis(2-hydroxy-4-n-propoxyphenyl)ethane-1,2-dione (13c)
Figure 2.26: $^{13}$C NMR of 1,2-bis(2-hydroxy-4-n-propoxyphenyl)ethane-1,2-dione (13c)
Figure 2.27: Mass Spectrum of 1,2-bis(2-hydroxy-4-n-propoxyphenyl)ethane-1,2-dione (13c)
Figure 2.28: $^1$H NMR of 1,2-bis(4-hydroxy-3,5-diisobutylphenyl)ethane-1,2-dione (13d)
Figure 2.29: $^{13}$C NMR of 1,2-bis(4-n-butoxy-2-hydroxyphenyl)ethane-1,2-dione (13a)
Figure 2.30: Mass Spectrum of 1,2-bis(4-butoxy-2-hydroxyphenyl)ethane-1,2-dione (13d)
Figure 2.31: $^1$H NMR of 1,2-bis(4-n-hexyloxy-2-hydroxyphenyl)ethane-1,2-dione (13e)
Figure 2.32: $^{13}$C NMR of 1,2-bis(4-hexyloxy-2-hydroxypheny)ethane-1,2-dione (13c)
Figure 2.33: Mass Spectrum of 1,2-bis(4-n-hexyloxy-2-hydroxyphenyl)ethane-1,2-dione (13e)
Figure 2.34: $^1$H NMR of 1,2-bis(2-hydroxy-4-n-octyloxyphenyl)ethane-1,2-dione (13f)
Figure 2.35: $^{13}$C NMR of 1,2-bis(2-hydroxy-4-n-octyloxyphenyl)ethane-1,2-dione (13f)
Figure 2.36: Mass Spectrum of 1,2-bis(2-hydroxy-4-n-octyloxyphenyl)ethane-1,2-dione (13f)
Figure 2.37: $^1$H NMR of 1,2-bis(4-n-decyloxy-2-hydroxyphenyl)ethane-1,2-dione (13g)
Figure 2.38: $^{13}$C NMR of 1,2-bis(4-n-decyl oxy-2-hydroxy phenyl)ethane-1,2-dione (13g)
Figure 2.39: Mass Spectrum of 1,2-bis(4-decyloxy-2-hydroxyphenyl)ethane-1,2-dione (13g)
Figure 2.40: $^1$H NMR of 1,2-bis(4-n-decyloxy-2-hydroxyphenyl)ethane-1,2-dione (13b)
Figure 2.41: $^{13}$C NMR of 1,2-bis(4-dodecylxyloxy)-2-hydroxyphenyl)ethane-1,2-dione (13h)
**Figure 2.42:** Mass Spectrum of 1,2-bis(4-n-dodecyloxy-2-hydroxyphenyl)ethane-1,2-dione (13h)
Figure 2.43: HPLC Chromatogram of pure chlorpyrifos without irradiation

Figure 2.44: HPLC Chromatogram of chlorpyrifos (without photostabilizer) after irradiation

Figure 2.45: HPLC Chromatogram of chlorpyrifos with 13a (1:1) after irradiation
Figure 2.46: HPLC Chromatogram of chlorpyrifos with $13b$ (1:1) after irradiation

Figure 2.47: HPLC Chromatogram of chlorpyrifos with $13c$ (1:1) after irradiation

Figure 2.48: HPLC Chromatogram of chlorpyrifos with $13d$ (1:1) after irradiation
**Figure 2.49:** HPLC Chromatogram of chlorpyrifos with 13e (1:1) after irradiation

**Figure 2.50:** HPLC Chromatogram of chlorpyrifos with 13f (1:1) after irradiation

**Figure 2.51:** HPLC Chromatogram of chlorpyrifos with 13g (1:1) after irradiation
Figure 2.52: HPLC Chromatogram of chlorpyrifos with $13h(1:1)$ after irradiation

Figure 2.53: HPLC Chromatogram of chlorpyrifos with $13h(1:0.1)$ after irradiation

Figure 2.54: HPLC Chromatogram of chlorpyrifos with $13h(1:0.3)$ after irradiation
Figure 2.55: HPLC Chromotagram of chlorpyrifos with $^{13}$h (1:0.5) after irradiation

Figure 2.56: HPLC Chromotagram of chlorpyrifos with $^{13}$h (1:0.7) after irradiation
2.7 References


