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STUDIES ON THE PHOTOCHEMICAL STABILITY OF
ORGANOPHOSPHORUS INSECTICIDES FOR TEXTILE MOTHPROOFING

By

BERNARD W. MADDEN B.Sc.(HONS.), B.Sc.(Ed.)

Being a thesis submitted for the
Degree of Master of Science
at Deakin University, December, 1980
DEAKIN UNIVERSITY

CANDIDATE'S CERTIFICATE

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ACKNOWLEDGEMENTS

The work described in this thesis was carried out under the direction of Dr. I.M. Russell and Dr. F.W. Jones, Principal Research Scientists, C.S.I.R.O. Division of Textile Industry and Dr. J.E. Moir, Lecturer in Organic Chemistry, Deakin University. To them I offer my sincere thanks for their guidance, advice and encouragement.

The majority of this work was performed at the C.S.I.R.O. Division of Textile Industry. I am grateful to Dr. D. Taylor, Chief of the Division, for extending to me full use of the Division's facilities and to all the members of the mothproofing group for their valued co-operation and many useful discussions. In particular I wish to thank Mrs. C. Nunn, for the performance of the biological tests.

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The light stability of 0,0-diethyl-0-(4-ethylthiophenyl)phosphorothioate, a parent structure of a new class of fibre-reactive organophosphorus insectproofing agents for use on wool textiles was extensively examined. The rate of degradation of 0,0-diethyl-0-(4-ethylthiophenyl)phosphorothioate in polar and non-polar solution and on wool upon irradiation by simulated sunlight was investigated using high performance liquid chromatography. The major photodegradation products in each case were correlated with the HPLC retention times of synthetically prepared compounds. The main product formed was the sulphoxide, 0,0-diethyl-0-(4-ethylsulphinylphenyl)phosphorothioate, whose insecticidal activity against the major textile pests was shown to be similar to that of the parent compound. In polar solution a polar product which could not be identified was formed. Both 4-ethylsulphinylphenol and 4-ethylsulphonylphenol were found on wool but not in solution. The effect of various ultraviolet stabilizers on the rate of photodegradation of 0,0-diethyl-0-(4-ethylthiophenyl)phosphorothioate was also examined. Ultraviolet absorbers of the 2-hydroxybenzophenone and 2-hydroxybenzotriazole classes conferred the best protection in each case. However, on wool typical wool dyes applied at conventional levels were also effective.
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1. INTRODUCTION

Textile pests cause much damage to raw and manufactured wool goods. Hartley et al [1] calculated that the progeny from a single female clothes moth if unchecked could consume approximately 100 lb. of wool after 280 days.

The textile pests chiefly responsible for damage are

(a) The Common Clothes Moth (*Tineola bisselliella*)
(b) The Case Bearing Clothes Moth (*Tinea pellionella, Tinea metonella* and *Tinea dubiella*)
(c) The White-tip Clothes Moth or Tapestry Moth (*Trichophaga tapetzella*)
(d) The Brown House (False Clothes) Moth (*Hofmannophila pseudospretella*)
(e) The Furniture Beetle (*Anthrenus flavipes*)

Of these, *Tineola bisselliella* is regarded as the single most important species. The adult moth itself does not do any damage, serving only to reproduce the species. The actual damage is done by the larvae which feed on animal fibres, after hatching from the eggs laid by the female moths. Ultimately they become pupae (the inactive stage of the insects' life-cycle) where they are transformed from larvae to adults. In nature, these insects fill a valuable ecological niche, having developed a unique ability to digest keratinized proteins (animal horn, skin, fur, hoofs), the normally indigestible parts of prey other predators cannot digest.

1.1 HISTORY OF COMMERCIAL MOTHPROOFING

The first commercial mothproofing process was developed as a result of
the early work of Meckbach [2]. From the observation that green
coloured materials were often resistant to moth attack it was found
that Martius yellow (2,4-dinitro-1-naphthol), a component of some
green dyes, had mothproofing properties. Attempts to produce a range
of mothproofing dyes failed and eventually it was discovered that
colourless inorganic compounds containing fluorine would mothproof
wool [2,3]. The first of several fluorine-containing mothproofers, the
Eulans, were marketed in 1920 but these are not used today because of
their potential toxicity to humans and their lack of persistence under
many conditions of normal use.

Between 1928 and 1939 several halogenated and sulphonated aromatic
compounds (1, 2, 3) were introduced. These behaved as colourless
dyestuffs and, when applied from an acid dyebath, were almost completely
exhausted, the sulphonic group conferring substantivity to the wool fibre
as well as water solubility. Insecticidal activities were generally low
and large applications were required, although Mitin FF (3) is still in
commercial use.
From this work in 1937 the remarkable properties of dichlorodiphenyl
trichloroethane (DDT) [4] were discovered in the Basle laboratories
of J.R. Geigy S.A. Considerable resistance to attack on wool was
conferred by very small amounts (of the order of 0.03% of fabric
weight (o.f.w.)) of DDT [4] although to survive losses during
laundering and due to sunlight larger quantities were considered
desirable [3, 5, 6].
In the late 1950's another chlorinated hydrocarbon, dieldrin (5), was found to be effective when applied to wool from an aqueous emulsion in an acid dyebath [7]. It did not react with wool but some of it penetrated the fibres. At the recommended application rate of 0.05% o.f.w. on wool it was cheap and rapidly became widely used throughout the world. Because of its high insecticidal activity the small amount applied was sufficient not only to mothproof the wool initially but also to provide protection against the losses associated with normal dry cleaning and laundering. However dyebath exhaustion under some conditions was not complete and since the mid 1960's there has been increasing concern for the effects of dieldrin on the environment [8]. In addition resistant insect strains have developed in Australia and in consequence it has been recommended that dieldrin no longer be used for mothproofing [9,10].

In Australia, Eulan WA New (6) and Mitin LA (7) replaced dieldrin as the major mothproofing agents even though they were much more expensive.
If any resistant insect strains were to develop they would become uneconomical since application rates would need to be increased accordingly. In order to reduce potential problems of cross resistance it is desirable that new mothproofing agents ought to be unrelated structurally and in their mode of action to those currently in use. This pre-requisite probably excludes all highly chlorinated diphenyl ethers, sulphonamides and diphenyl amines developed by Ciba Geigy and Bayer [11-23] as well as halogenated salicylanilides and brominated hydrocarbons as investigated by McPhee [24,25].

1.2. ALTERNATIVE MOTHPROOFING TECHNIQUES

1.2.1 ANTIFEEDANTS

Certain organotin compounds have general insecticidal [26] and antifeeding properties [27] and their use for mothproofing has been
examined [28,29]. Although triphenyltin chloride provided durable and effective mothproofing [30-32], it was not compatible with some anionic dyes and economic problems precluded it from commercial application.

Thiourea and certain of its derivatives were claimed to possess textile mothproofing properties in several patents issued around 1930 [33-35]. However it has since been found [36] that their exhaustion onto wool and consequent substantivity was poor. To overcome this problem a fibre-reactive group was attached to phenylthiourea so that this compound became chemically bound to the wool when applied under suitable conditions [37]. Although demonstrating the principle that insecticides can be bound to wool without loss of activity the substituted phenylthioureas were active inhibitors only of clothes moth feeding and were relatively ineffective against carpet-beetle larvae. In addition, rates of application to wool were too high (1% o.f.w.) for the fibre-reactive phenylthiourea to be commercially useful.

1.2.2 ANTIMETABOLITES
Antimetabolites have been defined as antagonistic structural analogues of metabolites which are essential in some phase of the life process [38]. Pence [39-42] suggested the application of antimetabolites for mothproofing of wool and claimed that imidazole, an antimetabolite of histamine, was effective at a 1% application on wool. This has since been disputed by Bry and McDonald [43]. Sulphanilamide and other sulphonamides, benzimidazole, pyridine-3- sulphonic acid and alkyl 2- thiazolines suggested as antimetabolites by Pence were not active enough to be of commercial value. In addition, most had poor fastness to washing and
1.2.3 FIBRE MODIFICATION
It was suggested by Linderstrom-Lang and Duspiva [44] that the unique ability of the textile pests to digest wool was probably due to the presence in their intestinal tract of a reductive enzyme system capable of breaking the disulphide bond in wool. It is this special linkage which is largely responsible for the insolubility and strength of wool fibres. As a result several attempts were made to replace some of these bonds with a different linkage which would be indigestible to the larvae [1, 45-55]. Unfortunately it has been found that modification of the fibre usually changes the desirable properties of the wool and such processes have not been used commercially.

1.2.4 SURFACTANTS
Surfactants, both cationic and anionic, have been shown to possess mothproofing properties [56-61] although they tend to be species specific and possess poor fastness to repeated washings and dry cleanings [56-58]. For effective and durable control of all species high levels of application were required and soiling, especially on carpets, was a problem [58]. Additionally, cationic surfactants were incompatible with anionic dyes and surfactants generally used for wool dyeing [61].

1.2.5 AGRICULTURAL INSECTICIDES
1.2.5.1 CARBAMATES
Carbamic acid esters have been shown to be important commercial insecticides [62] and are considered selective in their performance [63-65]. However they were found to be unsatisfactory for mothproofing
because they were unable to withstand the conditions of application and use [66]. This was believed to be due mainly to poor hydrolytic stability in the dye-bath. An attempt was made to improve the stability of certain active hydroxaryl and aminoaryl carbamates by preparing their fibre-reactive derivatives but this caused all activity to be lost [67].

1.2.5.2 PYRETHROIDS
Relatively safe but active synthetic pyrethroids have been recently developed for domestic and agricultural purposes and these have been examined for mothproofing usage [68-80]. Most synthetic pyrethroids were too unstable in light and air for industrial mothproofing although several were suitable as short term protectants [69-73]. Several new photostable synthetic pyrethroids [81,82] including permethrin [78,79], NRDC-143 [75,77,80], WL-43479, S-5602 and S-3206 [80] may be suitable for industrial mothproofing depending on cost effectiveness and ecological factors. One promising report [79] showed that permethrin could be applied to wool in the dye-bath at a concentration of 0.04 - 0.09% o.f.w. with most common dye types and was also compatible with several flameproofing and shrinkproofing treatments.

1.2.5.3 ORGANOPHOSPHORUS INSECTICIDES
Of the alternatives to dieldrin for textile mothproofing, organophosphorus compounds have probably received the greatest attention. In the 1930's independent groups in England and at I.G. Farben in Germany started intensive studies of the toxicity of organophosphorus compounds. By 1944, the German group had synthesized about 200 organophosphorus compounds, some of which are still used today as
insecticides. Organophosphorus compounds have been so widely investigated because their wide variation in chemical structure (Fig. 1.2.1) leads to substantial variations in chemical stability and biological activity. None have so far been found with the necessary combination of stability, activity, and durability essential for commercial application for mothproofing [66, 83-90].

1.3 BIOLOGICAL ACTIVITY OF ORGANOPHOSPHORUS INSECTICIDES

1.3.1 MODE OF ACTION

Organophosphorus esters are toxic to insects because of their ability to attack the nervous system.

When an electric nerve impulse reaches the end of an axon it causes a chemical transmitter to be released from the vesicles. This transmitter migrates to the receptor on the postsynaptic membrane of another neuron or muscle fibre causing depolarization of the membrane. A further electric nerve impulse is then initiated.

In insects, acetylcholine is the transmitter in the synapses of the central nervous system. Immediately after binding to the receptor the acetylcholine is hydrolyzed into inactive acetic acid and choline by the enzyme acetylcholinesterase in the synaptic junction. This hydrolysis of acetylcholine by acetylcholinesterase is essential to allow the postsynaptic membrane to return to its initial state.

It is widely accepted that organophosphorus insecticides poison insects by their inhibition of acetylcholinesterase. The enzyme inhibition results in accumulation of acetylcholine in the synaptic
Figure 1.2.1 General formula for organophosphorus insecticides

\[
\begin{array}{c}
R' \quad O(S) \\
\downarrow \\
\downarrow \\
P \\
R'' \quad R'''
\end{array}
\]

- \( R' \) and \( R'' \): usually alkoxy or alkylamino groups
- \( R''' \): the 'leaving group' often derived from an acid
- \( R' \) may be an alkyl group
cleft causing abnormal excitation of the nervous system which leads to severe and often lethal deterioration of the insect.

1.3.2 STRUCTURE-ACTIVITY RELATIONSHIP IN ACETYLCHOLINESTERASE INHIBITION

In general, organophosphorus esters containing a readily displaceable group are good acetylcholinesterase inhibitors. In particular, O,O-diethyl-O-(substituted-phenyl)phosphates are found to be useful acetylcholinesterase inhibitors, their activity being influenced by the effect of the substituent on the lability of the P-O phenyl bond. Phenyl phosphate esters with strong electron attracting substituents (e.g. NO₂, CN) on the benzene ring are strong inhibitors of acetylcholinesterase. acetylcholinesterase inhibiting activity increasing with electron withdrawing character [91]. This is because the ester more readily undergoes nucleophilic substitution on phosphorus as the P-O phenyl bond becomes more deficient in electron density.

Thioether substituted phenyl compounds have greater insecticidal activity than expected and it has been found that the substituent can be transformed to a more electron withdrawing one by oxidation of the sulphur moiety to the sulphoxide or sulphone. This may occur either in the environment or in the insect's gut [92-95].

Similarly, organophosphorous esters containing a thiophosphoryl group (P=S) can be transformed into more active inhibitors of acetylcholinesterase by oxidation to their oxo-analogs [96]. However the increase in activity varies greatly with the overall structure of the inhibitor. For example, there is a 3,000-fold difference between the anticholin-
esterase activity of cyclohexyl methylphosphonofluoridate and its thiono analog whereas the difference for pinacolyl methylphosphonofluoridate and its thiono analog is only 3-fold [96]. Obviously other factors, besides the poor electron withdrawing ability of the sulphur atom compared with the oxygen atom, need also to be taken into account.

1.4 FIBRE-REACTIVE INSECTICIDES

Organophosphorus insecticides on wool may be lost by laundering, volatilization, chemical degradation or by photochemical breakdown and in some cases both volatilization and photochemical breakdown were shown to be major routes [89]. In principle, it should be possible to prevent photodegradation and volatility losses by covalently bonding the insecticide to wool. Additionally, this approach also offers the potential advantages of better human safety, improved dye-bath application, and improved durability and wash fastness and this approach has been extensively studied at CSIRO Division of Textile Industry.

Since their discovery more than twenty years ago reactive dyes capable of covalently bonding with cellulose have enjoyed considerable commercial success. Reactive dyes for the acid dyeing of wool were soon developed and other fibre-reactive compounds have been suggested including fibre-reactive softeners [97]. Attempts were made to apply this technology to the mothproofing field [98,99] since it was anticipated that improvements in durability would result. Compound 8 was claimed to mothproof wool when applied from a boiling, slightly acidic bath [98]. The molecule reacted with wool via the active vinyl sulphone (9) obtained after elimination of the phosphate ester group. Johnson [99] used formaldehyde to bond chlorinated phenols onto wool.
Both approaches were of doubtful commercial value, requiring application of large quantities of material.

Organophosphorus insecticides are probably the most promising class of insecticides for fibre-reactive use because they possess a relatively broad spectrum of activity against textile pests, several of them have very high activity at low application rates which is necessary for economic viability and they seem less susceptible to small structural changes than other classes of insecticides. A complication in designing fibre-reactive insecticides for wool, which does not exist for reactive dyes, was that the insect must be able to remove an insecticidally active substance from the wool. This active material must be in a lipid soluble form to be able to penetrate to the site of action in the insect. If the bond between insecticide and wool cannot be broken by enzymic cleavage of the wool during insect digestion the insecticide will be released still attached to an amino acid residue. Such polar groups prevent the insecticide from effectively penetrating the lipid barrier of the nervous system and thus reduce insecticidal activity. To overcome this complication, fibre-reactive organophosphorus insecticides incorporating a labile bond between the insecticide and the fibre-reactive group have been examined at CSIRO Division of
Textile Industry \[100\] and may become suitable for textile moth-proofing. The bond must be strong enough to survive boiling acid dye-bath application and alkaline washing.

Since it was anticipated that photochemical degradation would be one of the major causes of loss of these insecticides from wool the purpose of this present study was to provide an initial investigation of the photochemical stability of fibre-reactive organophosphorus insecticides which are based on the class of compounds represented by structure 10. There are problems in analysis of organophosphorus insecticides bonded

\[
\text{R} - \text{CO-O-CH}_2\text{CH}_2\text{S} - \text{OP(O)(OC}_2\text{H}_5\text{)}_2
\]

\[
\text{R} = \text{fibre-reactive group}
\]

10
do wool, because hydrolysis to break the fibre-insecticide bond will also destroy the organophosphorus group, so this study examined the photochemical stability of 0,0-diethyl-0-(4-ethylthiophenyl)phosphorothioate (11) as a model compound in order to examine the possible routes

\[
\text{C}_2\text{H}_5\text{S} - \text{OP(O)(OC}_2\text{H}_5\text{)}_2
\]

11
and mechanisms of degradation.
1.5 PHOTOCHEMICAL DEGRADATION OF INSECTICIDES

1.5.1 GENERAL

Environmental photochemistry is complicated because molecules may interact with many environmental components. For any photoreaction to occur a compound must absorb light energy either directly or through a photo-sensitizer present in the wool, leaf, soil, water or air or by reaction with a photo-excited molecule. Most important, however, is the fact that the energy available in ultraviolet light is of the same order as that needed for the breaking of bonds. In a survey [101] of the spectra of 76 pesticides, 29 were found to have no absorption bands above 290 nm and 25 had very weak absorption. It is known from observations in the field that some pesticides with no absorption as high as 290 nm (the lowest wavelength transmitted through the earth's atmosphere), e.g. dieldrin [102-104], do degrade in sunlight and in these cases the environment of the molecule plays an important part in their behaviour. Intra- and intermolecular reactions may occur and in the case of intermolecular reactions, solvent or other surrounding molecules may participate. Adsorption onto surfaces may change the maximum absorption wavelength and thus alter the energy required for photodecomposition. It has been reported [105] that paraquat with a sharp band in the ultraviolet spectrum at 257 nm shows a shift to 275 nm (broad) with increased ultraviolet absorption above 290 nm when adsorbed on soil particles. The effect of physical state and the molecular environment has been discussed by Plimmer [106] who measured the changes in ultraviolet spectrum of some pesticides on adsorption by silica gel in cyclohexane slurries. Hydrogen bonding and pH of the environment can also affect considerably the absorption spectrum with shifts to longer wavelength.
Many attempts to simulate the wavelength range and intensity of sunlight by using various light sources have been reviewed [107-109], but in general, investigators of pesticide breakdown have used single lamp sources. Mercury vapour arcs, both low and high pressure are commonly used. Low pressure mercury lamps produce most of their energy (90%) in a band at 253.7 nm whereas the medium pressure lamps show strong bands at 366 nm (16%), 313 nm (9.2%), 302 nm (4.6%), 296 nm (3.3%) with some emission below 290 nm (about 10%) and some in the visible wavelength region. Mercury-tungsten filament-fluorescent (MBTF) lamps have been used for the accelerated light-fastness testing of dyed fabrics since first proposed by Giles et al in 1969 [110]. Results have correlated very well with the results of actual outdoor exposure tests, with good reproducibility over an extended period of use on replicate samples [111], and in consequence a MBTF lamp was the major light source used in the present study.

1.5.2 ORGANOPHOSPHORUS INSECTICIDES

The photodegradation of organophosphorus insecticides has been increasingly investigated in recent years. Many workers [112-123] found that the major photodegradation pathway of phenylphosphorothioates involved the oxidative desulphuration of the P=S double bond and in several cases [114-116, 121, 123] aryl ester cleavage was also a prominent photodegradation route.

In contrast, alkylthiophenylphosphorothioates were shown [124-129] to photodegrade by oxidation of the alkylthio sulphur to sulphoxide and then sulphone derivatives. Ivie and Bull [124] exposed BAY NTN 9306, (0-ethyl-0-[4-methylthiophenyl]-S-propylphosphorodithioate), (12),
applied to cotton leaves and in water to sunlight. In addition to oxidation of the methylthio sulphur they determined that cleavage of the phosphorous-0-phenyl ester to phenolic compounds also occurred, although these compounds did not accumulate to any appreciable extent. They postulated that these phenols underwent additional degradation to more polar products which they were unable to characterize since these products did not co-chromatograph with any authentic standards available and could not be resolved successfully by GLC-mass spectrometry. Oxidative desulphuration of the P-S moiety was found to occur only to a limited extent and only after extended irradiation. Similar results were obtained with both sunlight and using artificial light with a pyrex filter to remove light of wavelength less than 280 nm. Photodegradative mechanisms were not postulated but Figure 1.5.1 shows the products which were characterized.

For fenthion (19), the sulphone (20) was the initial major degradation product (126). It was formed rapidly and was stable for several half-lives before starting to degrade or hydrolyze. In addition, the four other degradation products shown in Figure 1.5.2 were also formed as minor products increasing in concentration over several half-lives until eventually also decreasing in concentration. The oxon analogue (21) was formed in trace amounts only.

Mitchell et al (127) showed that the thioether groups in the alkyl side chains of phorate (25), disulphoton (26), and thiometon (27) were oxidized to the corresponding sulphoxides and sulphones upon ultraviolet irradiation. In addition, oxidation of the thiono sulphur of thiometon occurred. These results for phorate and disulphoton were subsequently

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O}_\text{S} & \quad \text{C}_2\text{H}_5\text{O}_\text{S} \\
\text{C}_2\text{H}_5\text{O} & \quad \text{C}_2\text{H}_5\text{O} \\
\text{S} & \quad \text{S} \\
\text{P-SCH}_2\text{SC}_2\text{H}_5 & \quad \text{P-SCH}_2\text{CH}_2\text{SC}_2\text{H}_5 \\
\text{C}_2\text{H}_5 & \quad \text{C}_2\text{H}_5 \\
\text{25} & \quad \text{26} \\
\text{P-SCH}_2\text{SC}_2\text{H}_5 & \quad \text{P-SCH}_2\text{CH}_2\text{SC}_2\text{H}_5 \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{27} & \quad \text{27}
\end{align*}
\]
Figure 1.5.1 Structures of BAY NIN 9306 (12) and its Characterized Photoproducts Formed During Sunlight Exposure as Surface Deposits or in Water
Figure 1.5.2 Fenthion and Five of its Photodegradation Products
confirmed [130, 131] and in addition the oxon analogue and the
sulphoxide and sulphone of the oxon analogue were shown to be formed
as minor products.

1.5.3 INHIBITION OF PHOTOCHEMICAL DEGRADATION

Although numerous products are available for the protection of polymers
against sunlight degradation ultraviolet stabilizers have been used
rarely for the protection of insecticides. An ultraviolet stabilizer
may retard photodegradation in two ways: (i) by absorbing most of the
ultraviolet light itself leaving little to be absorbed by the
substrate, or (ii), although absorbing little or no ultraviolet light
itself it may interact with the photoexcited substrate and transfer the
excitation energy to itself. If this transfer occurs before any other
reaction of the excited substrate molecule takes place, degradation of
the substrate may be prevented. For maximum effectiveness the ultra-
violet stabilizer must be able to dispose of its excitation energy in
some harmless way without undergoing some irreversible photochemical
change itself.

Salicylates were the first photostabilizers to be used technically [132].
However most of them turn yellow on exposure to ultraviolet light, thus
limiting their use. The most important members of this group are
resorcinol monobenzoate (28) and phenyl salicylate (29a), but
substituted aryl salicylates (29b) and diaryl terephthalates (30) or
isophthalates (31) are also effective stabilizers. These compounds all
have very low absorption in the solar ultraviolet region but after
sufficient sunlight exposure a light-catalyzed rearrangement occurs
that converts them to 2-hydroxybenzophenones [133] which are very
effective ultraviolet stabilizers.

Most of the 2-hydroxybenzophenones used as stabilizers are derivatives of 2,4-dihydroxybenzophenone (32a), 2,2',4-trihydroxybenzophenone (33a), and 2,2',4,4'-tetrahydroxybenzophenone (34a), with the most

important commercially being the 4-alkoxy-2-hydroxybenzophenones (32b).
These compounds absorb much more strongly in the solar ultraviolet region than do the salicylates.

2-Hydroxybenzotriazoles (35) have a somewhat higher ultraviolet absorbance than the 2-hydroxybenzophenones and have a steeper long-wavelength cutoff. Generally they are slightly better screening agents than the benzophenones.

Each of the stabilizers mentioned so far retards photodegradation according to the first mechanism mentioned above and are properly called ultraviolet-radiation absorbers or screening agents. Several nickel-containing compounds, although also absorbing strongly in the solar ultraviolet region, are generally believed to act by the second method and are usually called excited-state quenchers. Organometallic complexes containing paramagnetic metal ions were shown to be effective quenchers of excited states in solution photochemistry [134, 135]. The quenching efficiency of these chelates was largely governed by the nature of the organic ligand and it was shown that chelates with square planar structures were the most effective [136]. The nickel chelates, Ferro AM-101 (36), Cyasorb 1084 (37) and nickel dibutyl-dithiocarbamate (38) were shown to have industrial applications for polymers [132, 137, 138] and it was suggested that both mechanisms
probably operated to different extents in different polymer-chelate combinations [138].

\[
\begin{align*}
\text{36}
\end{align*}
\]

\[
\begin{align*}
\text{37}
\end{align*}
\]

\[
\begin{align*}
\text{38}
\end{align*}
\]
Antioxidants may also be used to inhibit photodegradation in polymers [139]. Generally antioxidants are divided into two main types, the amine and the phenolic, or nitrogen-free types. If antioxidants were able to prevent photodegradation of organophosphorus insecticides it would be expected that only the phenolic types would be commercially acceptable for industrial mothproofing since they are less prone to staining and discolouration compared with the amine types [140]. A typical phenolic antioxidant is represented by structure 39, in which $R'$, $R''$, and $R'''$ are either the same or different alkyl groups.

![Structure 39](image)

In this present project, members of each class of photodegradation inhibitors were tested for effectiveness in the photoprotection of compound 11.
2. EXPERIMENTAL

2.1 ANALYTICAL APPARATUS

2.1.1 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

2.1.1.1 ISOCRATIC MODE

The apparatus used consisted of:

pump Altex pump, model 100;
injector Rheodyne sample loop (20 μl);
column Analyses in iso-octane were carried out on a Spherisorb (Phase Separations Ltd., Deeside Industrial Estate, Queensferry, Clwyd, U.K.) stainless steel column (4.6 mm I.D. x 250 mm), prepacked with silica (5 μm);

Analyses in ethanol were carried out on a Du Pont stainless steel column (4.6 x 250 mm), pre-packed with Zorbax ODS (5-6 μm);
detector Hitachi variable wavelength ultraviolet spectrophotometer, model 100-10, fitted with an Altex flow cell, model 155-00.

2.1.1.2 GRADIENT MODE

The apparatus used consisted of:

pump Two Altex pumps, model 100;
injector Varian autosampler controlled by an Altex Model 420 microprocessor;
column Du Pont stainless steel (4.6 mm I.D. x 250 mm), pre-packed with Zorbax ODS (5-6 μm);
detector Perkin Elmer LC 55 variable wavelength ultraviolet spectrophotometer;
data processor Spectra Physics System I Computing Integrator.
or
Spectra Physics SP4100 Computing Integrator.

2.1.2 GAS CHROMATOGRAPHY
A Bendix 1500 series Gas Chromatograph fitted with a phosphorus-specific-flame photometric detector and a glass column (1.6 m) packed with Chromosorb W 80-120 mesh coated with 3% OV1 was used.

2.1.3 ULTRAVIOLET SPECTROSCOPY
Ultraviolet spectra were determined on a Varian Superscan 3 Ultraviolet-Visible Spectrophotometer.

2.1.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
Samples in deuterated chloroform were analyzed using a Varian 60A nuclear magnetic resonance spectrophotometer.

2.1.5 GAS CHROMATOGRAPHY - MASS SPECTROMETRY (GC-MS)
Samples were analyzed using a Finnigan 3500 series GC-MS.

2.1.6 LIGHT SOURCES
Two light sources were used.
1. A PCQ-X1 Photochemical Lamp (Ultraviolet Products, Inc., San Gabriel, Calif.) producing 80 to 90% of its irradiation at 253.7 nm.
2. A mercury vapour/tungsten filament/phosphor-coated fluorescent (MBTTF) lamp housed inside a fan ventilated box essentially as described by Fincher et al [111]. This light box was modified by extending one end by 20 cm and leaving the extension open at
the top to facilitate removal and addition of samples. The
temperature (32°C) 18 cm from the lamp where the samples were
situated was unaltered by the modification.

2.2 SYNTHETIC

2.2.1 4-Ethylthiophenol (40)

\[
\text{苯} \quad \text{NH}_4\text{SCN/Cl}_2 \quad \text{NCS-苯}
\]

\[
\begin{align*}
1. 2\text{NaOH} & \rightarrow \text{HS-苯} \quad 1. \text{NaOH} & \rightarrow \text{C}_2\text{H}_5\text{S-苯} \\
2. \text{HCl} & \quad \text{OH} & \quad 2. \text{C}_2\text{H}_5\text{I} & \quad \text{OH}
\end{align*}
\]

Sodium hydroxide (10.8 g) was dissolved in the minimum amount of water
necessary, stirred in ethanol (150 ml), and added to 4-mercaptophenol
(34.2 g, prepared according to the method of Consolidated Coal Company
[141] in 65% yield). Ethyl iodide (42.2 g) was added dropwise with
stirring at room temperature. The stirring was continued for 20 hours.
The solvent was evaporated, H\_2O (200 ml) added, and the mixture
extracted with toluene (200 ml). The organic phase was washed with H\_2O
(3 x 100 ml), dried over Na\_2SO\_4, and the solvent removed under reduced
pressure at 60°C to yield 4-ethylthiophenol (37.8 g, 90%), a yellow
oil which turned solid (m.p. 34 - 36°C) on cooling.
Element analysis
Calculated for C_8H_10O_S:  C 62.33;  H 6.49;  O 10.38;  S 20.8
Found:  C 62.10;  H 6.63;  O 10.17;  S 20.4

NMR analysis
7.0 δ, M, (4H);  2.8 δ, Q, (2H);  1.2 δ, T, (3H).

Mass spectral analysis
Principal peaks: m/e 27, 29, 39, 45, 53, 81, 97, 125, 126, 139, 153, 154.

2.2.2 0,0-Diethyl-0-(4-ethylthiophenyl)phosphorothioate (II)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{S} & \quad \text{(C}_2\text{H}_5\text{O})_2\text{P(S)Cl} \\
\text{K}_2\text{CO}_3 & \quad \rightarrow \\
\text{C}_2\text{H}_5\text{S}  & \quad \text{OP} \\
& \quad \text{OC}_2\text{H}_5 \\
& \quad \text{OC}_2\text{H}_5 \\
\end{align*}
\]

K_2CO_3 (4.4 g) was suspended in a solution of 4-ethylthiophenol (4.9 g) and diethylchlorothiophosphinate (7.1 g) in anhydrous acetonitrile (80 ml) and the mixture heated under reflux for 2 hours. The mixture was cooled, filtered, and the filtrate concentrated under reduced pressure. The residue was taken up in toluene (100 ml), extracted with NaOH (10%, 50 ml) and H_2O (3 x 50 ml), dried over Na_2SO_4, and the solvent removed under reduced pressure at 60°C to yield an oil (10.6 g). TLC on silica gel with a 1% methanol in dichloromethane running solvent, showed this product to be impure. The impurities were removed by heating the residue at 100°C under a vacuum of 0.1 mm Hg in a Buchi GKR-50 Ball oven whereupon II was obtained as a yellow oil, yield 7.5 g (77%).
Element analysis

Calculated for $C_{12}H_{19}O_3PS_2$: C 47.04; H 6.25; P 10.11; S 20.9

Found: C 47.31; H 6.16; P 10.20; S 21.1

NMR analysis

7.2 δ, M, (4H); 4.2 δ, M, (4H); 2.85 δ, Q, (2H); 1.2 δ, M, (9H)

Mass spectral analysis

Principal peaks: m/e 27, 29, 45, 65, 97, 125, 153.

2.2.3 4-Ethylsulphinylphenol (41)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{S} - \text{OH} & \xrightarrow{\text{NaOH}} \xrightarrow{\text{acetic anhydride}} \text{C}_2\text{H}_5\text{S} - \text{C} = \text{O} - \text{CH}_3 \\
& \xrightarrow{\text{H}_2\text{O}_2} \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_2\text{H}_5\text{S} - \text{C} = \text{O} - \text{OH}
\end{align*}
\]

4-Ethylthiophenol (5.0 g) was dissolved in aqueous NaOH (25%, 5 ml), the mixture was cooled to 0°C and acetic anhydride (3.3 g) added with vigorous stirring. The mixture was extracted with ether (100 ml) and the ether extract washed successively with NaOH (10%, 100 ml) and H$_2$O (100 ml), dried over Na$_2$SO$_4$ and the solvent removed to yield 4-ethylthiophenylacetate (4.3 g).

A methanolic solution (3 ml) of 4-ethylthiophenylacetate (1.0 g) containing 1 drop of aqueous H$_2$SO$_4$ (50%) was heated to 45°C and H$_2$O$_2$
(30%, 0.53 ml) added dropwise. The temperature rose to 50°C and the mixture was stirred at this temperature for 1 hour. Aqueous NaOH (10%, 5 ml) was added and the mixture stirred for 15 min. After acidification with dilute HCl to pH 3 the mixture was extracted with ethyl acetate (2 x 20 ml), the extract dried over Na₂SO₄ and the solvent removed to yield 4-ethylsulphonylphenol contaminated with a small amount of 4-ethylsulphonylphenol. 4-ethylsulphonylphenol (0.3 g, 35%) was collected as a white solid (m.p. 92 - 94°C) by liquid chromatography using methanol-dichloromethane (3:97).

**Element analysis**

Calculated for C₆H₁₀O₂S : C 56.45; H 5.92; O 18.80; S 18.8
Found : C 56.44; H 5.79; O 18.37; S 19.4

**NMR analysis**

7.3 δ, Q, (4H); 2.9 δ, Q, (2H); 1.1 δ, T, (3H); 14.8 δ, S, (1H)

**Mass spectral analysis**

Principal peaks : m/e 27, 29, 39, 45, 53, 65, 94, 97, 125, 126, 139, 140, 141, 142, 154, 170.

2.2.4 4-Ethylsulphonylphenol (42)
A solution of 4-ethylthiophenylacetate (2.0 g) in acetic acid (10 ml) was heated under reflux while H₂O₂ (30%, 2.2 ml) was added dropwise. After 4 hours the acetic acid was removed at 60°C under vacuum. The residue was dissolved in NaOH (10%, 10 ml), acidified with dilute HCl to pH 3 and extracted with ethyl acetate (20 ml). The extract was washed with saturated NaHCO₃ (10 ml), dried over Na₂SO₄ and the solvent evaporated to yield 4-ethylsulphophenylphenol as a yellow oil (1.5 g, 79%).

**Element analysis**

Calculated for C₈H₁₀O₃S: C 51.59; H 5.41; O 25.77; S 17.2

Found: C 51.53; H 5.37; O 25.20; S 17.9

**NMR analysis**

7.4 δ, Q, (4H); 3.1 δ, Q, (2H); 1.3 δ, T, (3H)

**Mass spectral analysis**

Principal peaks: m/e 27, 29, 38, 39, 42, 43, 64, 65, 93, 94, 109, 141, 156, 157, 186.

2.2.5 0,0-Diethyl-0-(4-ethylthiophenyl)phosphate (43)

\[ \text{C}_2\text{H}_5\text{S} \text{OH} \xrightarrow[\text{K}_2\text{CO}_3]{(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{Cl}} \text{C}_2\text{H}_5\text{S} \text{OC}_2\text{H}_5 \text{OC}_2\text{H}_5 \]  

43

K₂CO₃ (0.9 g) was suspended in a solution of 4-ethylthiophenol (1.0 g) and diethylchlorophosphate (1.12 g) in anhydrous acetonitrile (30 ml) and the mixture was stirred at 20°C for 36 hours. TLC analysis indicated that the reaction was incomplete and so the mixture was heated under
reflux for a further 2 hours. The mixture was filtered and the filtrate
diluted with toluene (30 ml) and washed successively with NaOH (10%,
30 ml) and H₂O (3 x 30 ml), dried over Na₂SO₄ and the solvent removed.
The residue (1.2 g) contained two compounds. O,O-Diethyl-O-(4-ethyl-
thiophenyl)phosphate was obtained as a yellow oil (0.5 g, 27%) by
liquid chromatography on silica gel using dichloromethane-hexane (4:1)
as eluting solvent.

**Element analysis**
Calculated for C₁₂H₁₉O₄PS : C 49.65; H 6.55; P 10.7; S 11.0
Found : C 49.75; H 6.64; P 11.2; S 10.8

**NMR analysis**
7.2 δ, M, (4H); 4.2 δ, M, (4H); 2.8 δ, Q, (2H); 1.2 δ, T, (9H)

**Mass spectral analysis**
Principal peaks : m/e 27, 29, 45, 81, 109, 125, 290.

2.2.6 O,O-Diethyl-O-(4-ethylsulphinylphenyl)phosphorothioate (44)

This compound was prepared (60% yield) as described previously [142]
and purified by liquid chromatography on silica gel using dichloro-
methane-methanol (99:1).
Element analysis
Calculated for C_{12}H_{19}O_4PS_2: C 44.71; H 5.94; P 9.6; S 19.9
Found: C 44.25; H 5.86; P 9.3; S 20.0

NMR analysis
7.5 δ, M, (4H); 4.3 δ, M, (4H); 2.8 δ, M, (2H); 1.3 δ, M, (9H)

Mass spectral analysis
Principal peaks: m/e 29, 65, 97, 109, 125, 141, 153, 293, 294, 322.

2.2.7 0,0-Diethyl-0-(4-ethylsulphinylphenyl)phosphate (45)

\[
\begin{align*}
\text{C}_2\text{H}_5\text{S} & \quad \text{O} \\
\text{OH} & \quad \xrightarrow{\text{K}_2\text{CO}_3} \\
\text{(C}_2\text{H}_5\text{O})_2\text{P(0)Cl} & \quad \text{O} \\
\text{C}_2\text{H}_5\text{S} & \quad \xrightarrow{\text{45}} \\
\text{O} & \quad \text{OC}_2\text{H}_5 \\
\text{OC}_2\text{H}_5 & \quad \text{OC}_2\text{H}_5
\end{align*}
\]

K_2CO_3 (0.18 g) was suspended in a solution of 4-ethylsulphinylphenol (0.2 g) and diethylchlorophosphate (0.2 g) in anhydrous acetonitrile (15 ml) and the mixture stirred at 20°C for 3 days. TLC analysis showed a considerable amount of unreacted 4-ethylsulphinylphenol. The mixture was heated under reflux for 4 hours. TLC analysis indicated incomplete reaction. Diethylchlorophosphate (0.05 g) was added to the mixture which was heated under reflux for a further 3 hours. TLC analysis still indicated incomplete reaction therefore more diethylchlorophosphate (0.05 g) was added and the mixture heated under reflux overnight and stirred at 20°C for a further 24 hours. Toluene (20 ml) and H_2O (20 ml) were added to the mixture and the toluene layer washed sequentially with aqueous Na_2CO_3 (10%, 20 ml) and H_2O (3 x 20 ml), dried over Na_2SO_4, and the
solvent removed. 0,0-Diethyl-0-(4-ethylsulphonylphenyl)phosphate (0.09 g, 25%), a yellow oil, was isolated from the residue by liquid chromatography on silica gel using dichloromethane-methanol (50:1).

**Element analysis**

Calculated for C₁₂H₁₅O₅PS : C 47.05; H 6.25; P 10.1; S 10.5

Found : C 46.45; H 6.12; P 10.3; S 10.6

**NMR analysis**

7.5 δ, M, (4H); 4.3 δ, M, (4H); 2.8 δ, M, (2H); 1.3 δ, M, (9H)

**Mass spectral analysis**

Principal peaks : m/e 27, 29, 81, 109, 140, 141, 221, 222, 249, 276, 277, 278, 290, 306.

2.2.8 0,0-Diethyl-0-(4-ethylsulphonylphenyl)phosphorothioate (46)

\[
\text{C}_2\text{H}_5\text{S} \quad \begin{array}{c}
\text{(C}_2\text{H}_5\text{O})_2\text{P(S)Cl} \\
\text{K}_2\text{CO}_3
\end{array} \rightarrow \text{C}_2\text{H}_5\text{SO} \quad \begin{array}{c}
\text{S} \\
\text{OC}_2\text{H}_5 \quad \text{OC}_2\text{H}_5
\end{array}
\]

46

K₂CO₃ (0.38 g) was suspended in a solution of 4-ethylsulphonylphenol (0.5 g) and diethylchlorothiophosphate (0.61 g) in anhydrous acetonitrile (30 ml) and the mixture stirred at 20°C for 7 hours. Toluene (30 ml) and H₂O (30 ml) were added to the mixture and the organic layer washed sequentially with aqueous NaOH (10%, 30 ml) and H₂O (3 x 30 ml), dried over Na₂SO₄, and the solvent removed. 0,0-Diethyl-0-(4-ethylsulphonylphenyl)phosphorothioate (0.6 g, 66%) was obtained.
from the residue as a yellow oil by liquid chromatography on silica gel using dichloromethane-methanol (99:1).

**Element analysis**

Calculated for $\text{C}_{12}\text{H}_{19}\text{O}_5\text{PS}_2$: C 42.59; H 5.66; P 9.2; S 19.0

Found: C 43.05; H 6.15; P 9.5; S 19.3

**NMR analysis**

7.7 δ, M, (4H); 4.2 δ, M, (4H); 3.1 δ, Q, (2H); 1.2 δ, M, (9H)

**Mass spectral analysis**

Principal peaks: m/e 27, 29, 63, 65, 77, 97, 109, 125, 141, 156, 202, 338.

2.2.9. 0,0-Diethyl-0-(4-ethylsulphonylphenyl)phosphate (47)

This compound was prepared in an analogous manner as 46 using diethyl-chlorophosphate (0.51 g). 0,0-Diethyl-0-(4-ethylsulphonylphenyl) phosphate (0.2 g, 22%) was obtained as a yellow oil after liquid chromatography on silica gel with dichloromethane-methanol (20:1).

**Element Analysis**

Calculated for $\text{C}_{12}\text{H}_{19}\text{O}_6\text{PS}$: C 44.72; H 5.94; P 9.6; S 10.0

Found: C 44.58; H 5.89; P 9.1; S 10.2
NMR analysis

7.7 δ, M, (4H); 4.2 δ, M, (4H); 3.1 δ, Q, (2H); 1.3 δ, M, (9H).

Mass spectral analysis

Principal peaks: m/e 27, 29, 63, 64, 65, 77, 81, 99, 109, 127, 141, 173, 196, 201, 224, 293, 294, 322.

2.3 PHOTODEGRADATION OF O,O-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE IN SOLUTION

2.3.1 CALIBRATION CURVES

Calibration curves for analysis of II were determined by injecting 20 μl aliquots of solutions with concentrations ranging from 20 to 50 mg L⁻¹ into the HPLC system. System A (Table 2.3.1) was used for analysis of II in iso-octane and system B for II in ethanol.

TABLE 2.3.1 HPLC conditions

<table>
<thead>
<tr>
<th>Mobile phase</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%(v/v) isopropanol in iso-octane</td>
<td>0.1%(v/v) acetonitrile in 2.5 x 10⁻⁴ M phosphate buffer(pH 2.5)</td>
<td>1%(v/v) iso-propanol in dichloromethane</td>
<td></td>
</tr>
<tr>
<td>Flow rate (ml/min)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Detector wavelength (nm)</td>
<td>260</td>
<td>260</td>
<td>220</td>
</tr>
</tbody>
</table>
### Gradient System

<table>
<thead>
<tr>
<th>Mobile phase</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol-aqueous acetonitrile (30:70)</td>
<td>Aqueous acetonitrile 2.5 x 10^{-4} M</td>
<td></td>
</tr>
<tr>
<td>2.5 x 10^{-4} M</td>
<td>phosphate buffer (pH 2.5)</td>
<td>phosphate buffer (pH 2.5)</td>
</tr>
<tr>
<td>Initial concentration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% (v/v) methanol-acetonitrile</td>
<td>40% (v/v) acetonitrile</td>
<td></td>
</tr>
<tr>
<td>Concentration after 20 min. linear gradient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90% (v/v) methanol-acetonitrile</td>
<td>90% (v/v) acetonitrile</td>
<td></td>
</tr>
<tr>
<td>Time held at maximum (min)</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>Time to decrease to minimum concentration (min)</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>Time held at minimum (min)</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Flow rate ml/min</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Detector wavelength (nm)</td>
<td>220</td>
<td>220</td>
</tr>
</tbody>
</table>

#### 2.3.2 IRRADIATION OF 0,0-DIETHYL-0-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE (11) IN SOLUTION

#### 2.3.2.1 USING A PCQ-XI LAMP

Solutions of 11 (100 mg l^{-1}) in either iso-octane (80 ml) or ethanol (80 ml) were placed in quartz or pyrex test-tubes and stirred continuously while irradiated by the PCQ-XI lamp. Aliquots (1 ml) were removed and analyzed for undegraded 11 using HPLC system A for the iso-octane solutions and system B for the ethanol solutions.

#### 2.3.2.2 USING A MBIF EXPOSURE BOX

A solution of 11 (100 mg l^{-1}) in iso-octane (100 ml) was placed in a
round bottom pyrex flask (200 ml), the flask stoppered and placed in
the unmodified MBTF exposure box so that the centre of the flask was
15 cm from the centre of the lamp and the solution stirred during
irradiation. Aliquots (200 μl) were removed and analyzed for
undegraded 11 by HPLC system A.

A solution of 11 (100 mg l⁻¹) in either iso-octane (10 ml) or ethanol
(10 ml) was added to each of six screw top pyrex vials (12.5 cm x
1.75 cm id.) or six Bausch and Lomb Spectronic 20 Colorimeter test-
tubes which were placed in a curved test-tube holder 15 cm from the
centre of the lamp of the modified MBTF exposure box. The solutions
were irradiated and analyzed for undegraded 11 using HPLC systems A
and B for the iso-octane and ethanol solutions respectively.

2.3.3 DETECTION OF THE PHOTODEGRADATION PRODUCTS
2.3.3.1 PHOTODEGRADATION IN ISO-OCTANE

Gradient elution HPLC was used to monitor the formation of photo-
degradation products of 11 in solution and the rate of photodegradation
of compounds 40 to 47. Aliquots (250 μl) of the irradiated iso-octane
solutions of the appropriate compounds (100 mg l⁻¹) were diluted with
iso-octane (1.0 ml) and analyzed by HPLC system D.

2.3.3.2 PHOTODEGRADATION IN ETHANOL

Aliquots (250 μl) of irradiated ethanolic solutions of the appropriate
compounds (100 mg l⁻¹) were diluted with 1.0 ml of a 50:50 (v/v)
acetonitrile/2.5 x 10⁻⁴ M phosphate buffer (pH 2.5) solution and
analyzed by HPLC system E.
2.3.4 ATTEMPTS TO IDENTIFY THE POLAR PHOTODEGRADATION PRODUCT

Solutions of II (100 mg L⁻¹) in ethanol (6 ml) were placed in each of 6 Bausch and Lomb Spectronic 20 Colorimeter test-tubes and irradiated in the MBTF exposure box for 10 hours, the solutions combined and concentrated to 0.5 ml on a rotary evaporator. The polar component of this solution was isolated by HPLC on a "reverse" phase column and an eluting solvent of 5% (v/v) acetonitrile/2.5 x 10⁻⁴ M formate buffer (pH 2.5). The solution was applied to the column in 20 µl aliquots, the collected polar fractions combined, concentrated to 0.1 ml on a rotary evaporator and analyzed by GC-MS.

A larger quantity of polar products was obtained by irradiating an ethanolic solution (200 ml) of II (1 g L⁻¹) in a round bottom Pyrex flask (500 ml) in the MBTF exposure box for 100 hours. The solution was concentrated, the polar fractions collected as above, and analyzed by GC-MS.

2.3.5 PHOTODEGRADATION IN THE PRESENCE OF ULTRAVIOLET STABILIZERS

A solution of II (100 mg L⁻¹) in iso-octane (6 ml) or ethanol (6 ml) was irradiated in the first position in the curved test-tube rack in the MBTF exposure box, while solutions (6 ml) of II (100 mg L⁻¹) containing varying concentrations of the appropriate ultraviolet stabilizers were irradiated in the other five positions. The concentration of undegraded II was determined using either HPLC system A or B, and the formation of degradation products was monitored using system D or E.
2.4 PHOTODEGRADATION OF 0,0-DIETHYL-O-(4-ETHYLTHIOPHENYL)-PHOSPHOROTHIOATE (11) ON WOOL

2.4.1 WOOL
A soap-scoured, undyed, plain-weave fabric of 135 g/m², made from 64s-quality merino wool, was used.

2.4.2 APPLICATION OF 0,0-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE (11) TO WOOL

11 was applied to wool from an aqueous emulsion in an Ahiba Turbowat laboratory dyeing apparatus using a 20:1 liquor : wool ratio. The wool (25 g) was wet out, wound onto a dyeing beam, placed in an aqueous solution (450 ml) of ammonium sulphate (1.2 g) and acetic acid (1 ml) and heated to 40°C. This solution was circulated through the wool for 5 minutes. An aqueous emulsion of the insecticide and the appropriate ultraviolet stabilizer (prepared by emulsifying 11 (50 mg), the appropriate amount of ultraviolet stabilizer, Alkanate CS (50 mg), Teric N 13 (50 mg), and xylene (300 mg) in water (50 ml) on a high speed laboratory blender) was added. At this stage any pre-dissolved dye was also added. The bath was heated to 100°C over 30 minutes and held at this temperature for 30 minutes. The treated fabrics were removed, rinsed in cold water (600 ml) for 10 minutes, hydroextracted, and air dried.

2.4.3 ANALYSIS OF 0,0-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE (11) ON WOOL

2.4.3.1 BY HPLC
Treated wool (0.20 g), hydrochloric acid (5%, 5 ml), iso-octane (1.1 ml), and dichloromethane (0.9 ml) were placed in a sealed ampoule
and heated at 70°C for 2 hours in a shaking water bath. The ampoule was cooled, opened, iso-octane (3.0 ml) was added, the mouth of the ampoule covered with Parafilm and the ampoule shaken vigorously. The organic phase (20 μl) was injected into the liquid chromatograph using system A. Standard solutions of 11 in an 18% (v/v) solution of dichloromethane in iso-octane were employed to calibrate the instrument.

2.4.3.2 BY GAS-LIQUID CHROMATOGRAPHY

11 was converted to 0,0-diethyl-S-methylphosphorothiolate by the following procedure and determined gas chromatographically. Duplicate samples of wool (0.200 g) were dissolved in aqueous NaOH (2.5 M, 4 ml) at 70°C for 20 minutes. The mixtures were cooled, neutralized with H₂SO₄ (1M, 5 ml), buffered with Na₂B₂O₄.H₂O (2 g), treated with excess dimethyl sulphate (200 μl) and shaken vigorously. After 30 minutes the 0,0-diethyl-S-methylphosphorothiolate was extracted into toluene (3 ml) and determined gas chromatographically using the following conditions:

- Column temperature: 185°C
- Detector temperature: 200°C
- Injection port temperature: 200°C
- Carrier gas: N₂ at 30 ml min⁻¹

The amount of 11 present on the wool was estimated by comparison with the simultaneous analysis of samples of wool containing known amounts of 11 which were applied to the wool by padding known concentrations of 11 onto the wool from acetone.
2.4.4 ANALYSIS OF PHOTODEGRADATION PRODUCTS

The photodegradation products were determined by extracting the wool as described in Section 2.4.3.1 and the extracts analyzed by HPLC system C.

2.4.5 ANALYSIS OF SPENT DYE-BATH AND RINSE LIQUORS [80]

Aliquots of spent dye-bath (80 ml) or rinse liquors (80 ml) were saturated with anhydrous Na$_2$SO$_4$, stirred with a 20% (v/v) solution of dichloromethane in iso-octane (8.0 ml) and the organic phase analyzed by HPLC system A.

2.4.6 PHOTODEGRADATION AND VOLATILITY OF O,O-DIETHYL-O-(4-ETHYLTHIO-PHENYL)PHOSPHOROTHIOATE [11] WHEN APPLIED TO WOOL

Wool samples (160 mm x 60 mm) were suspended vertically on the front and back of aluminium plates (160 mm x 60 mm) which were placed 18 cm from the lamp in an unmodified MBTF exposure box such that only the sample on the front of a plate received light exposure. The temperature at the point of exposure was 32 ± 2°C. Samples of wool (0.2 g) from the front and back positions were analyzed as described in Sections 2.4.3.1 and 2.4.4.

2.4.7 INSECT-TESTING

Insect feeding damage of the treated wool was determined by the fabric-weight-loss method as described in AATCC Standard Test Method 24-1963 [143] using the larvae of the common clothes moth (Tineola bisselliella), the case bearing clothes moth (Tinea pellionella), and the furniture carpet beetle (Anthrenus flavipes). According to this standard, wool is considered insectproof if the feeding damage does not exceed 8 mg provided that the feeding damage to the controls exceeds 30 mg.
3. DISCUSSION AND RESULTS

3.1 QUANTITATIVE ANALYSIS OF THE ORGANOPHOSPHORUS INSECTICIDES

Until recently residual organophosphorus insecticides were determined in the environment almost exclusively by thin-layer chromatography or gas chromatography. However, thin-layer chromatography is slow and difficult to quantitate and gas chromatography is not generally reliable because of thermal instability of organophosphorus compounds [144]. Recently, high performance liquid chromatography (HPLC) has been widely used in the analysis of organophosphorus insecticides [145 - 151]. Because HPLC is generally a sensitive and reliable method for the determination of trace amounts of organophosphorus compounds and has the ability to analyse polar degradation products without derivatization it was used in the present study.

Two types of columns were used - a "normal" phase column and a "reverse" phase column. Compounds deposited on a normal phase column are eluted in order of increasing polarity using either an eluting solvent of constant composition - isocratic mode - or a solvent mixture which is changed with time to uniformly increase the polarity of the eluting solvent during the chromatogram - gradient elution. In the present work normal phase columns were used in the isocratic mode using an eluting solvent mixture of iso-propanol in either iso-octane or dichloromethane. This allowed direct injections of the irradiated solutions of 0,0-diethyl-0-(4-ethylthiophenyl)-phosphorothioate (11) in iso-octane. Since the injecting solvent was of a lower polarity than the eluting solvent reproducible peak areas were obtained with no peak distortion [152, 153].
Compounds deposited on a reverse phase column are eluted in order of decreasing polarity. Generally a gradient elution system is used such that the polarity of the solvent is decreased with time. In the present study mixtures of water, acetonitrile and methanol were used.

In order to maximize the sensitivity of the analysis procedure a variable wavelength ultraviolet detector was used. Maximum response to 11 was obtained when the detector was set at a wavelength of 260 nm. Linear calibration graphs of peak height versus concentration were obtained (correlation co-efficient 0.9991) at least up to 500 mg L\(^{-1}\) of 11. The detection limit (10 times baseline noise) for 11 was approximately 0.05 mg L\(^{-1}\) at 260 nm using a 20 µl injection loop.

3.2 IRRADIATION OF O,O-DIETHYL-0-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE IN SOLUTION

To most closely simulate the factors responsible for ultraviolet degradation of organophosphorus insecticides in sunlight it was necessary to use equipment which simulated sunlight conditions especially in the ultraviolet region. This could be done by using a lamp with a spectral distribution similar to that of sunlight or by using filters in conjunction with a lamp. Although filters with sharp UV cut-off
are readily available, several workers [154 - 156] have found it simpler to use different types of glass as the containers for solution photolysis. Pyrex, Jena Glas, A.C.I. glass and Pierce sample bottles were found to give zero transmittance below 290, 280, 300 and 294 nm, respectively (Fig. 3.2.1). Although the ultraviolet region of the solar spectrum extends from 4 to 400 nm, radiation below about 290 nm is almost completely filtered out by the atmosphere, and the total amount that does reach the earth’s surface represents less than 7% of the total solar radiation [157]. In this study pyrex containers were used.

The first light source examined was a PCQ-X1 Photochemical Lamp; 80 to 90% of the radiation for this source was at 253.7 nm and the total light output of its four lamps was approximately 5.6 watts. Pyrex glass effectively removed most of this low wavelength light. For example, when an ethanolic solution of I was irradiated in a quartz test-tube (which transmitted light of 253.7 nm) degradation was almost complete after 4.5 hours; however, in a pyrex test-tube negligible degradation was observed (Table 3.2.1). To follow the degradation of II by light resembling the solar spectrum a light source with more intense radiation above 290 nm was required.

This was obtained by using a mercury vapour/tungsten filament/ phosphor-coated fluorescent (MBTF) lamp. This MBTF lamp, had a phosphor coating as well as a tungsten filament, and therefore added visible light to the mercury vapour spectrum while reducing ultraviolet radiation [110]. Hindson and Southwell [158] found these lamps to be satisfactory for the accelerated light-fastness testing of dyed fabrics and they have been included in the DEF (Aust.) Standard
Figure 3.2.1 Light transmittance of glass
TABLE 3.2.1 Photodegradation of an Ethanol Solution of \textit{11} in Quartz and Pyrex Test-Tubes using a PCQ-XI Photochemical Lamp.

<table>
<thead>
<tr>
<th>Exposure Time (hr)</th>
<th>% of \textit{11} remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Quartz</td>
</tr>
<tr>
<td>0.5</td>
<td>12</td>
</tr>
<tr>
<td>1.0</td>
<td>7.5</td>
</tr>
<tr>
<td>1.5</td>
<td>4.5</td>
</tr>
<tr>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>3.5</td>
<td>0.6</td>
</tr>
<tr>
<td>4.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

5037 as an acceptable means of simulating sunlight for accelerated light fastness testing.

When solutions of \textit{11} in pyrex screw-cap vials were irradiated by a MBTF lamp inside a fan-ventilated exposure box as described by Fincher et al [111] a much faster rate of photodegradation occurred than when the PCQ-XI Photochemical Lamp was used. In subsequent experiments the fan-ventilated box was modified to facilitate sample handling.

The photodegradation of \textit{11} in solution followed first order kinetics. This was shown for solutions ranging from 50 to 400 mg l$^{-1}$ which displayed a linear relationship between the logarithm of the concentration and the time of irradiation up to at least three half-lives (Fig. 3.2.2), with the half-life of \textit{11} within this range being
Figure 3.2.2 Typical $\log_{10} (\text{conc})$ vs time relationship for photodegradation of II over three half-lives.
independent of concentration. The half-lives and correlation coefficients were calculated with a TI 59 calculator. (See Appendix for program). Typically, photodegradation of 11 in either ethanol or iso-octane gave correlation coefficients between 0.9904 and 0.9995 (Fig. 3.2.3 and 3.2.4) for the plots of $\log_{10}$ (concentration) versus time.

Rates of degradation were dependent on sample size. Large volume samples (100 ml volume in 200 ml flask) gave a half-life of 16.8 hours (correlation coefficient 0.9957), whilst several small volume pyrex vials placed the same distance from the lamp in the MBTF exposure box gave half-lives of approximately 7 hours. Although this faster rate of degradation using the 10 ml capacity vials was more convenient, there were unacceptable variations from vial to vial (Table 3.2.2) caused by the alignment of the vials with respect to the asymmetric tungsten filament (Fig. 3.2.5) and by variations in the UV transparency of the vials.

TABLE 3.2.2 Percentage of 11 Remaining in 10 ml Capacity Pyrex Vials after Irradiation by a MBTF lamp

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>Vial 1</th>
<th>Vial 2</th>
<th>Vial 3</th>
<th>Vial 4</th>
<th>Vial 5</th>
<th>Vial 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>76</td>
<td>73</td>
<td>71</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>62</td>
<td>61</td>
<td>57</td>
<td>64</td>
<td>62</td>
<td>61</td>
</tr>
<tr>
<td>8</td>
<td>42</td>
<td>36</td>
<td>31</td>
<td>42</td>
<td>40</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>32</td>
<td>27</td>
<td>22</td>
<td>34</td>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>14</td>
<td>16</td>
<td>13</td>
<td>8</td>
<td>16</td>
<td>16</td>
<td>9</td>
</tr>
</tbody>
</table>
Figure 3.2.3 Plot of $\log_{10}(\text{conc})$ vs time for photodegradation of \text{II} in solution giving a correlation co-efficient of 0.9904

Figure 3.2.4 Plot of $\log_{10}(\text{conc})$ vs time for photodegradation of \text{II} in solution giving a correlation co-efficient of 0.9995
Figure 3.2.5 View of MBTF lamp exposed to solutions
Better results were obtained by using matched Bausch and Lomb Spectronic 20 Colorimeter test-tubes placed in the same position in the test-tube rack for each experiment and aligned towards the lamp in exactly the same manner for each experiment. In this way, in two successive experiments in which 100 mg l⁻¹ solutions of 11 in iso-octane were irradiated in six of these test-tubes, the variation in the half-life of 11 from tube to tube was greatly reduced than when using previous containers. But more importantly, the rate of degradation obtained in a particular test-tube was reproducible and could be related to that obtained in another tube in another position by a constant factor. For example, the half-lives of 11 in five of the test-tubes were 1.02, 1.10, 1.18, 1.17 and 1.19 times greater than the half-life calculated for the iso-octane solution of 11 in the sixth test-tube (Table 3.2.3). Similar results were obtained for the photodegradation

<table>
<thead>
<tr>
<th>Test-Tube</th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half-life</td>
<td>Factor by</td>
</tr>
<tr>
<td></td>
<td>(Correlation</td>
<td>which half-</td>
</tr>
<tr>
<td></td>
<td>Co-efficient)</td>
<td>life exceeds</td>
</tr>
<tr>
<td></td>
<td>that for test</td>
<td>that for test</td>
</tr>
<tr>
<td></td>
<td>tube #1</td>
<td>tube #1</td>
</tr>
<tr>
<td>1</td>
<td>8.43 (0.9994)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8.62 (0.9995)</td>
<td>1.02</td>
</tr>
<tr>
<td>3</td>
<td>9.28 (0.9993)</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>9.97 (0.9977)</td>
<td>1.18</td>
</tr>
<tr>
<td>5</td>
<td>9.90 (0.9990)</td>
<td>1.17</td>
</tr>
<tr>
<td>6</td>
<td>10.07 (0.9994)</td>
<td>1.19</td>
</tr>
</tbody>
</table>

**TABLE 3.2.3** Comparison of Half-Lives of 100 mg l⁻¹ Solutions of 11 in Iso-octane in Bausch and Lomb Spectronic 20 Colorimeter Test-tubes.
of \( \text{II} \) in ethanol although correction factors for particular test-tubes were slightly different from those obtained using iso-octane (Table 3.2.4).

**TABLE 3.2.4** Comparison of Half-Lives of 100 mg l\(^{-1} \) Solutions of \( \text{II} \) in Ethanol in Bausch and Lomb Spectronic 20 Colorimeter Test-Tubes

<table>
<thead>
<tr>
<th>Test-Tube</th>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half-life (Correlation Co-efficient)</td>
<td>Factor by which half-life exceeds that for test-tube #1</td>
</tr>
<tr>
<td>1</td>
<td>8.81 (0.9990)</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>8.85 (0.9937)</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>9.72 (0.9989)</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>10.41 (0.9991)</td>
<td>1.13</td>
</tr>
<tr>
<td>5</td>
<td>9.98 (0.9982)</td>
<td>1.25</td>
</tr>
<tr>
<td>6</td>
<td>11.03 (0.9988)</td>
<td>1.25</td>
</tr>
</tbody>
</table>

To allow for possible variations in mains voltage and lamp intensities, standard solutions of \( \text{II} \) were always irradiated in test-tube one in position one and rates of degradation were calculated relative to this test-tube, after correcting for tube position by use of the appropriate correction factor determined as above. The daily variations in half-life of \( \text{II} \) in test-tube one are shown in Table 3.2.5.

### 3.2.1 PHOTODEGRADATION PRODUCTS

By comparison with previous studies [112-131] of the photodegradation of related organophosphorus compounds a number of compounds were
TABLE 3.2.5 Daily Variations in Half-Life of 100 mg L⁻¹ Solutions of II in Iso-octane and Ethanol

<table>
<thead>
<tr>
<th>Iso-octane</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Half-life (hr)</strong></td>
<td><strong>Correlation Co-efficient</strong></td>
</tr>
<tr>
<td>8.06</td>
<td>0.9982</td>
</tr>
<tr>
<td>8.65</td>
<td>0.9982</td>
</tr>
<tr>
<td>8.43</td>
<td>0.9994</td>
</tr>
<tr>
<td>7.16</td>
<td>0.9971</td>
</tr>
<tr>
<td>7.59</td>
<td>0.9979</td>
</tr>
<tr>
<td>7.24</td>
<td>0.9935</td>
</tr>
<tr>
<td>7.89</td>
<td>0.9963</td>
</tr>
<tr>
<td>6.67</td>
<td>0.9990</td>
</tr>
<tr>
<td>7.16</td>
<td>0.9989</td>
</tr>
<tr>
<td>8.30</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

Mean half-life 7.72 hr
Maximum variation 1.05 hr
Mean half-life 9.13 hr
Maximum variation 1.74 hr

considered to be possible photodegradation products of II (Fig. 3.2.6). These compounds were prepared and the HPLC conditions required for their analysis determined. Maximum detector response was obtained for these compounds at 220 nm. Under these conditions II could be detected at 0.07 mg L⁻¹. Because of the widely differing polarities of these compounds determination of them in irradiated solutions of II was most conveniently carried out using gradient elution on a reverse phase column. For analysis of ethanolic solutions of II a linear gradient from 40% to 90% acetonitrile in aqueous phosphate buffer (NaH₂PO₄, 2.5 x 10⁻⁴ M, pH 2.5) over 20 minutes was used. Retention times are
Figure 3.2.6 Possible photodegradation products of 11

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41

42
given in Table 3.2.6. Iso-octane was immiscible with the initial eluting solvent of 40% acetonitrile in aqueous phosphate buffer. Therefore when 11 was photodegraded in iso-octane it was necessary to use different analysis conditions. In these cases a linear gradient from 40% to 90% of a mixture of acetonitrile and methanol (7:3) in aqueous phosphate buffer (NaH₂PO₄, 2.5 x 10⁻⁴ M, pH 2.5) over 20 minutes was used.

The photodegradation products formed by the irradiation of 11 were identified on the basis of comparative retention times because they were present in such small quantities that it was not feasible to collect and identify them by other conventional means. In iso-octane the only degradation product detected was 0,0-diethyl-0-(4-ethyl-sulphinylphenyl)phosphorothioate (44). The oxidation of the sulphide to a sulphone group has been observed to be a major photodegradation pathway in other studies involving compounds containing an alkylthio substituent in the para position of a phenylphosphorodithioate [124, 125].

The amount of 44 detected in irradiated solutions of 11, both ethanolic and in iso-octane, did not correspond to the amount of 11 degraded. For example, at the half-life of an irradiated solution of 11 (100 mg L⁻¹) in iso-octane only 25 mg L⁻¹ of 44 was detected and in ethanol only 18 mg L⁻¹ was found. However, in ethanol an unknown amount of a very polar product with a retention time of 149 seconds was found. If it was assumed that this polar product had similar extinction co-efficient at the detector wavelength used as 11, then only a small amount of it was present. An attempt was made to isolate this polar product for identification by irradiating a more concentrated ethanolic solution of
TABLE 3.2.6 Retention Times of Potential Photodegradation Products of 11 in Ethanol using Gradient Elution HPLC.

<table>
<thead>
<tr>
<th>Compound Number</th>
<th>$R_I$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>567</td>
</tr>
<tr>
<td>41</td>
<td>204</td>
</tr>
<tr>
<td>42</td>
<td>228</td>
</tr>
<tr>
<td>43</td>
<td>903</td>
</tr>
<tr>
<td>44</td>
<td>742</td>
</tr>
<tr>
<td>45</td>
<td>304</td>
</tr>
<tr>
<td>46</td>
<td>897</td>
</tr>
<tr>
<td>47</td>
<td>388</td>
</tr>
</tbody>
</table>
(1 g l⁻¹) in a round bottom Jena Glas flask for several half-lives. However reverse phase HPLC using water-formic acid buffer (2.5 x 10⁻⁴ M) as mobile phase revealed the formation of four additional polar products. These five polar products could not be satisfactorily resolved by HPLC or identified by GC-MS. Other workers [124, 159] have also shown the formation of polar products from the photodegradation of organophosphorus pesticides and insecticides both on surfaces and in solution and have been unsuccessful in identifying them. Ohkawa et al [123] found several very polar products after photodegradation of fenitrothion (47) by both sunlight and ultraviolet light. They postulated that these polar

![Chemical Structure]

products were polymeric humic acids.

When compounds containing an alkylthio substituent in the para position of a phenylphosphorodithioate were irradiated for a prolonged time, in excess of two half-lives, oxidation of the sulphide group was observed to produce not only the sulphone but also the sulphone [124,125]. Cleavage of the phosphorus ester to give the corresponding phenol was also observed.

For O-phenylphosphorothioates lacking on alkylthio substituent on the phenyl ring the major degradation pathway was usually found to be oxidative desulphuration and aryl ester cleavage [123, 160, 161].
To elucidate the mechanism of photolytic breakdown the expected initial degradation products were irradiated under the same conditions as 11. Only 4-ethylthiophenol (40) and 0,0-diethyl-O-(4-ethylthiophenyl)phosphate (43) degraded (Fig. 3.2.7). Of the stable compounds only 44 was detected during irradiation of 11 indicating that the others were not involved in the degradation. In ethanol, but not in iso-octane, compound 40 (half-life 2.8 hours, correlation co-efficient 0.9993) and compound 43 (half-life 15.2 hours, correlation co-efficient 0.9995) both produced a polar degradation product which had the same retention time as the unidentified polar product formed as a photolysis product of 11.

It is possible that compounds 40 and 43 were formed during the photodegradation of 11 in ethanol and then rapidly degraded to the polar product as shown below:

If these products were involved in consecutive first order reactions
Figure 3.2.7 Graphs of $\log_{10} (\text{conc})$ vs time for ethanolic solutions (100 mg L$^{-1}$) of 40 and 43
their maximum concentrations would be given by

\[
(C)_{\text{max}} = a \left( \frac{k_2}{k_1 - k_2} \right)
\]

where \(a\) is the initial concentration of \(11\), and \(k_1\) and \(k_2\) represent the rate constants for the two reactions. From Fig. 3.2.7, \(k_2\) for \(40\) was 0.25 hr\(^{-1}\) and \(k_2\) for \(43\) was 0.046 hr\(^{-1}\).

The minimum detectable concentrations of both \(40\) and \(43\) were 0.05 mg l\(^{-1}\). Therefore since these compounds were not detected under the conditions used to analyze irradiated solutions of \(11\)

\[
(C_{40})_{\text{max}} \leq 3.2 \times 10^{-7} \text{ mole } l^{-1}
\]

\[
(C_{43})_{\text{max}} \leq 1.7 \times 10^{-7} \text{ mole } l^{-1}
\]

Substituting in equation 1,

\[
k_1(40) \leq 2.5 \times 10^{-4} \text{ hr}^{-1}
\]

\[
k_1(43) \leq 2.4 \times 10^{-5} \text{ hr}^{-1}
\]

These rate constants are small in comparison with the rate constant of \(7.8 \times 10^{-2} \text{ hr}^{-1}\) for the overall photodegradation of \(11\) in ethanol. Therefore although \(40\) and \(43\) may be formed during the photodegradation of \(11\) in ethanol they would only represent a minor pathway.

The major photodegradation pathway of \(11\) was concluded to involve only oxidation of the sulphide group to sulphone group in iso-octane while in ethanol a polar product was produced in addition to the sulphone (Figs. 3.2.8 and 3.2.9). In both solutions the detected
Figure 3.2.8 Photodegradation pathways for 11 in iso-octane

Figure 3.2.9 Photodegradation pathways for 11 in ethanol
photodegradation products accounted for less than 50% of the loss of
indicating substantial photodegradation to unobserved products.

3.2.2 THE EFFECT OF ULTRAVIOLET STABILIZERS ON THE PHOTODEGRADATION OF
0,0-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE

3.2.2.1 RATE OF PHOTODEGRADATION IN PRESENCE OF ULTRAVIOLET STABILIZERS
Several classes of ultraviolet stabilizers of varying modes of action
are available for protection against photodegradation. These include
ultraviolet absorbers and quenchers, and antioxidants.

Ultraviolet absorbers are believed to act both by absorbing energy from
excited bonds in the irradiated compound and by screening the irradiated
compound from ultraviolet light [163] and thus they need to absorb light
at the wavelength causing the degradation. Typical quenchers do not need
high absorptions at these wavelengths [132]. For most quenchers light
excitation from the ground state to the lowest triplet is virtually
forbidden and the resulting absorption is only weak. For energy transfer,
these selection rules do not hold and hence the quencher can deactivate
the excited chromophore in the irradiated compound at energy levels at
which it is transparent to light. The quencher is then raised to an
excited state and can only reduce photodegradation if it can dissipate
this accumulated energy harmlessly. The mechanism of action of anti-
oxidants during photo-oxidation is similar to that involved in the
inhibition of oxidation [139] where they react with generated radicals
either by chain transfer or termination.

The structures of the ultraviolet stabilizers used are given in Table
3.2.7 and their effect on the rate of photodegradation of II is shown in Table 3.2.8.

<table>
<thead>
<tr>
<th>UV Stabilizer</th>
<th>Mode of Action</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyasorb UV 24</td>
<td>UV absorber</td>
<td><img src="image1.png" alt="Structure" /></td>
</tr>
<tr>
<td>Cyasorb 207</td>
<td>UV absorber</td>
<td><img src="image2.png" alt="Structure" /></td>
</tr>
<tr>
<td>Cyasorb 1084</td>
<td>Quencher</td>
<td><img src="image3.png" alt="Structure" /></td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>UV absorber</td>
<td><img src="image4.png" alt="Structure" /></td>
</tr>
<tr>
<td>Irganox 415</td>
<td>Anti-oxidant</td>
<td><img src="image5.png" alt="Structure" /></td>
</tr>
<tr>
<td>Substance</td>
<td>Type</td>
<td>Molecular Formula</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>Anti-oxidant</td>
<td>( \text{(CH}_3 \text{)}_3 \text{C} \text{HO-CH}_2\text{CH}_2\text{COOC}_18\text{H}_37 )</td>
</tr>
<tr>
<td>Irganox 1093</td>
<td>Anti-oxidant</td>
<td>( \text{(CH}_3 \text{)}_3 \text{C} \text{HO-CH}_2\text{POC}_18\text{H}_37 )</td>
</tr>
<tr>
<td>Plastinox 425</td>
<td>Anti-oxidant</td>
<td>( \text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4 \text{HO-CH}_2\text{OH} \text{C(CH}_3 \text{)}_3 )</td>
</tr>
<tr>
<td>Phenyl salicylate</td>
<td>UV Absorber</td>
<td>( \text{C}_6\text{H}_5\text{CO-CH}_2\text{C}_6\text{H}_4 )</td>
</tr>
<tr>
<td>3,5-Di-t-butyl-4-hydroxy benzoic acid</td>
<td>Anti-oxidant</td>
<td>( \text{HO-CH}_2\text{C}=\text{COOH} \text{(CH}_3 \text{)}_3 \text{C} )</td>
</tr>
<tr>
<td>Resorcinol monobenzoate</td>
<td>UV absorber</td>
<td></td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>2,6-di-t-butyl-4-hydroxy methyl phenol</td>
<td>Anti-oxidant</td>
<td></td>
</tr>
<tr>
<td>Benzophenone</td>
<td>Photosensitizer</td>
<td></td>
</tr>
</tbody>
</table>

The most effective ultraviolet stabilizers were Tinuvin 320 and Cyasorb UV 24. Their effectiveness increased with concentration, but not in a linear fashion (Table 3.2.9).
<table>
<thead>
<tr>
<th>UV stabilizer (100 mg l(^{-1}))</th>
<th>Iso-octane</th>
<th></th>
<th></th>
<th></th>
<th>Ethanol</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>corrected half-life (hr)</td>
<td>correlation co-efficient</td>
<td>relative half-life (hr)</td>
<td>corrected half-life (hr)</td>
<td>correlation co-efficient</td>
<td>relative half-life (hr)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>54.2</td>
<td>0.9987</td>
<td>7.6</td>
<td>50.6</td>
<td>0.9910</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>53.9</td>
<td>0.9940</td>
<td>7.4</td>
<td>59.3</td>
<td>0.9968</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyasorb 1084</td>
<td>20.7</td>
<td>0.9909</td>
<td>2.9</td>
<td>25.1</td>
<td>0.9969</td>
<td>2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyasorb 207</td>
<td>8.0</td>
<td>0.9910</td>
<td>1.1</td>
<td>31.7</td>
<td>0.9982</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irganox 415</td>
<td>7.8</td>
<td>0.9961</td>
<td>1.1</td>
<td>8.3</td>
<td>0.9968</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irganox 1076</td>
<td>8.0</td>
<td>0.9983</td>
<td>1.1</td>
<td>7.0</td>
<td>0.9976</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irganox 1093</td>
<td>8.6</td>
<td>0.9993</td>
<td>1.1</td>
<td>7.4</td>
<td>0.9995</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plastinox 425</td>
<td>12.0</td>
<td>0.9977</td>
<td>1.7</td>
<td>8.5</td>
<td>0.9983</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenyl salicylate</td>
<td>18.6</td>
<td>0.9972</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,5 Di-t-butyl-4-hydroxybenzoic acid</td>
<td>7.5</td>
<td>0.9914</td>
<td>1.0</td>
<td>9.4</td>
<td>0.9983</td>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resorcinol monobenzoate</td>
<td>7.3</td>
<td>0.9948</td>
<td>1.0</td>
<td>7.2</td>
<td>0.9905</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6 Di-t-butyl-4-hydroxymethyl phenol</td>
<td>9.6</td>
<td>0.9943</td>
<td>1.3</td>
<td>10.9</td>
<td>0.9972</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzophenone</td>
<td>2.8</td>
<td>0.9978</td>
<td>0.4</td>
<td>3.2</td>
<td>0.9995</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Concentration of \( \text{I1} \) : 100 mg l\(^{-1}\)
TABLE 3.2.9 Effect of Various Concentrations of Tinuvin 320 and Cyasorb UV 24 on the Half-Life of 100 mg L⁻¹ Solutions of 11

<table>
<thead>
<tr>
<th>UV Stabilizer</th>
<th>Concentration mg/L⁻¹</th>
<th>Relative Half-life in isooctane</th>
<th>Relative Half-life in ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tinuvin 320</td>
<td>25</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>50</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>100</td>
<td>7.6</td>
<td>7.4</td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>200</td>
<td>15.4</td>
<td>10.3</td>
</tr>
<tr>
<td>Tinuvin 320</td>
<td>400</td>
<td>24.8</td>
<td>15.8</td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>25</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>50</td>
<td>4.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>100</td>
<td>7.4</td>
<td>7.2</td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>200</td>
<td>10.2</td>
<td>8.7</td>
</tr>
<tr>
<td>Cyasorb UV 24</td>
<td>400</td>
<td>19.1</td>
<td>15.3</td>
</tr>
</tbody>
</table>

The UV spectrum of a solution of 11 in iso-octane is shown in Figure 3.2.10. It can be seen that only a limited amount of light of wavelength greater than 290 nm is absorbed by 11, but this amount is sufficient to cause photodegradation. The UV spectra of the ultraviolet stabilizers used are shown in Figures 3.2.11 – 3.2.14 which indicate that the stabilizing effect is approximately related to the ultraviolet absorption above 290 nm. That is, with the exception of phenyl salicylate, those ultraviolet stabilizers with strong absorbances above 290 nm are those which most effectively stabilize 11 against
Figure 3.2.10  UV spectrum of II in iso-octane (10 mg l\(^{-1}\)). Path length 1 cm.

Absorbance

Figure 3.2.11  UV spectra of 10 mg l\(^{-1}\) solutions of Cyasorb UV 24, Cyasorb 207, Cyasorb 1084 in iso-octane. Path length 1 cm.

Absorbance
Figure 3.2.12 UV spectra of 10 mg l⁻¹ solutions of Irganox 415, Irganox 1076 and Irganox 1093 in iso-octane. Path length 1 cm.

Absorbance

Wavelength (nm)

0.5

Irganox 415

Irganox 1093

Irganox 1076

290

350

410

Figure 3.2.13 UV spectra of 10 mg l⁻¹ solutions of Tinuvin 320, Plastinox 425, and 3,5-di-t-butyl-4-hydroxybenzoic acid in iso-octane. Path length 1 cm.

Absorbance

3,5 di-t-butyl-4-hydroxybenzoic acid

Wavelength (nm)

0.5

290

350

410
Figure 3.2.14 UV spectra of 10 mg l⁻¹ solutions of Benzophenone, Resorcinol monobenzoate, Phenyl salicylate, and 2,6-di-t-butyl-4-hydroxymethyl phenol in iso-octane. Path length 1 cm.
photodegradation.

However, it is not possible to predict the protective ability of ultraviolet stabilizers based solely on comparative absorption spectra. Other factors which should be considered include the compatibility of the ultraviolet stabilizers with the organophosphorus insecticide, whether the ultraviolet stabilizer is destroyed by ultraviolet radiation, or whether the absorption spectra of the irradiated compound and of the stabilizer change during the photodegradation process, and finally whether the degradation products of the compound of interest absorb light [164].

2-Hydroxybenzophenones, such as Cyasorb UV 24, and 2-hydroxybenzotriazoles such as Tinuvin 320 are believed to act not just as ultraviolet screening agents but also by transferring energy from excited bonds in the irradiated compound [165-168]. Because both the 2-hydroxybenzophenones and the 2-hydroxybenzotriazoles can form internal hydrogen bonds the energy transfer mechanism for both has been considered [138] to involve rapid tautomerism of the excited states (Fig. 3.2.15).

As expected, benzophenone accelerated the rate of photodegradation. It is a potent photosensitizer and the triplet state formed in high efficiency by intersystem crossing from the initial singlet excitation product is a powerful oxidizing agent [132] which can abstract hydrogen atoms from all but the most stable substrates.
Figure 3.2.15 Photostabilization mechanisms of 2-hydroxybenzophenones and 2-hydroxybenzotriazoles
The remaining compounds tested had much less effect on the light stability of II. This was probably due to their very low absorption in the solar ultraviolet region and their inability to act as energy transfer agents. The ultraviolet absorbers, resorcinol monobenzoate and phenyl salicylate, are used to protect polymers and degrade rapidly to 2-hydroxybenzophenones [133, 138] which are the active stabilizers. When these compounds were used in the present studies no formation of 2-hydroxybenzophenone could be detected by HPLC after 10 hours of irradiation by which time more than 50% of II had been degraded.

Cyasorb 207, which acts principally as an ultraviolet absorber, was more efficient in ethanol than in iso-octane. This was probably due to the increased potential to form hydrogen bonds in this solvent which would increase the probability of rapid tautomerism of the excited states.

The quencher, Cyasorb 1084, protected II from photo-degradation to a much less extent than Cyasorb UV 24 or Tinuvin 320 but was two to three times more effective than the antioxidants and Cyasorb UV 207. Cyasorb 1084 is a nickel chelate which is effective by both a quenching and a screening mechanism [138]. The quenching mechanism would be expected to be more important than UV screening because of the low absorbance in the solar ultraviolet region (Fig. 3.2.11).

Each of the antioxidants used in the present studies offered only poor photoprotection to II although each had previously been found effective to varying degrees in inhibiting oxidation of polymers by ultraviolet irradiation or by direct reaction with active oxygen species. A recent
study [169] found that 2,6-di-t-butyl-4-hydroxymethylphenol photo-
degraded rapidly.

It is apparent from these results that to enhance the light stability
in solution of organophosphorus compounds similar to 11, ultraviolet
absorbers of either the 2-hydroxybenzophenone or 2-hydroxybenzotriazole
type which absorb strongly in the solar ultraviolet region, and
can harmlessly transfer energy from the triplet state of an excited
bond by forming internal hydrogen bonds, should be used.

3.2.2.2 PHOTODEGRADATION PRODUCTS IN PRESENCE OF ULTRAVIOLET
STABILIZERS

None of the ultraviolet stabilizers altered the nature of the degradation
products in either iso-octane or ethanol. However the most effective
ultraviolet stabilizers, Tinuvin 320 and Cyasorb UV 24, inhibited the
formation of the unidentified polar product in the ethanolic solution
until several hours after 44 was first detected (Fig. 3.2.16),
indicating that this polar product probably formed by a minor degradation
pathway.

3.3 PHOTODEGRADATION OF O,O-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHORO-
THIOATE ON WOOL

3.3.1 APPLICATION OF INSECTICIDE TO WOOL

Compound 11 (0.2% of fabric weight) was applied to a wool fabric by
exhaustion of an aqueous emulsion in a laboratory dyeing apparatus
(Section 2.4.2)

3.3.2 APPLICATION OF INSECTICIDE TO WOOL WITH ULTRA-VIOLET
STABILIZERS
Figure 3.2.16  Concentration vs time relationships of (a) 11 (x), 44 (o) and unidentified polar product (□) in an irradiated ethanolic solution of 11 containing Cyasorb UV 24 (100 mg L⁻¹). (b) 11 in unstabilized ethanolic solution (□).
A range of ultraviolet stabilizers (Table 3.3.1) was applied to wool together with \( \text{II} \) (0.2% o.f.w.) in the same manner as for application of \( \text{II} \) alone (Section 3.3.1). Analysis of the application liquors after exhaustion (Table 3.3.1) indicated that only a very small amount of \( \text{II} \) remained in the dye-bath.

<table>
<thead>
<tr>
<th>Wool Treatment</th>
<th>% of applied II remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2% II</td>
<td>1.2</td>
</tr>
<tr>
<td>0.2% II + 0.2% Cyasorb UV 24</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2% II + 0.8% Cyasorb UV 24</td>
<td>0.8</td>
</tr>
<tr>
<td>0.2% II + 0.05% Cyasorb UV 24</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2% II + 0.2% Tinuvin 320</td>
<td>0.2</td>
</tr>
<tr>
<td>0.2% II + 0.8% Tinuvin 320</td>
<td>0.2</td>
</tr>
<tr>
<td>0.2% II + 0.05% Tinuvin 320</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2% II + 0.2% Irganox 415</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2% II + 0.2% Benzophenone</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2% II + 0.2% 2,6-di-tert-butyl 4-hydroxy-methyl phenol</td>
<td>0.6</td>
</tr>
<tr>
<td>0.2% II + 0.2% Cyasorb UV 24 + 1% Lanasol red 5B dye</td>
<td>0.4</td>
</tr>
<tr>
<td>0.2% II + 1% Lanasol red 5B dye</td>
<td>0.4</td>
</tr>
</tbody>
</table>

3.3.3 ANALYSIS METHOD

Analysis of insecticides on wool has usually been carried out by extraction of the insecticide from the wool. A variety of methods has been used [80, 89, 170]. In the current work these methods were evaluated to determine the best for removal of II (Table 3.3.2). The highest recoveries (70% of calculated application) were obtained by
<table>
<thead>
<tr>
<th>Aqueous phase</th>
<th>Organic Phase</th>
<th>Time in 70°C Water Bath(hr)</th>
<th>% recovery of calculated application</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% HCl</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>55</td>
</tr>
<tr>
<td>5% HCl</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>57</td>
</tr>
<tr>
<td>5% HCl</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>59</td>
</tr>
<tr>
<td>5% HCl</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>5% HCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>59</td>
</tr>
<tr>
<td>5% HCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>61</td>
</tr>
<tr>
<td>5% HCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>60</td>
</tr>
<tr>
<td>5% HCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>60</td>
</tr>
<tr>
<td>5% HCl</td>
<td>iso-octane</td>
<td>1</td>
<td>33</td>
</tr>
<tr>
<td>5% HCl</td>
<td>iso-octane</td>
<td>2</td>
<td>44</td>
</tr>
<tr>
<td>5% HCl</td>
<td>CH₂Cl₂</td>
<td>2</td>
<td>48</td>
</tr>
<tr>
<td>5% HCl</td>
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<td>1</td>
<td>69</td>
</tr>
<tr>
<td>5% HCl</td>
<td>45% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>70</td>
</tr>
<tr>
<td>5% HCl saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>61</td>
</tr>
<tr>
<td>5% HCl saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>61</td>
</tr>
<tr>
<td>5% HCl saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>62</td>
</tr>
<tr>
<td>5% HCl saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>62</td>
</tr>
<tr>
<td>5% HCl saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>5% HCl saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>65</td>
</tr>
<tr>
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<td>65</td>
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<td>H₂O</td>
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<td>50</td>
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<tr>
<td>H₂O</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>55</td>
</tr>
<tr>
<td>H₂O</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>58</td>
</tr>
<tr>
<td>H₂O</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>51</td>
</tr>
<tr>
<td>1% HSO₃⁻</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>53</td>
</tr>
<tr>
<td>1% HSO₃⁻</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>51</td>
</tr>
<tr>
<td>1% HSO₃⁻</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>49</td>
</tr>
<tr>
<td>1% HSO₃⁻</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>52</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>59</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>59</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>56</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>10% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>58</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>63</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>iso-octane</td>
<td>1</td>
<td>33</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>iso-octane</td>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>45% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>63</td>
</tr>
<tr>
<td>1% HSO₃⁻, pH7</td>
<td>45% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>63</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>0.5</td>
<td>62</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>65</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with Na₂SO₄</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>65</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>1.5</td>
<td>60</td>
</tr>
<tr>
<td>1% HSO₃⁻, saturated with NaCl</td>
<td>20% CH₂Cl₂/isooctane</td>
<td>2</td>
<td>62</td>
</tr>
</tbody>
</table>

*11 was applied to the wool at 0.2% of fabric weight.
shaking the wool in a mixture of 5% hydrochloric acid and dichloromethane-isooctane (9:11) solution at 70°C for 2 hours.

Hoskinson and Russell [89] reported that when Chlorpyrifos was applied to wool at 100°C in an open dye-bath only 50% was found on the wool. They attributed this loss to steam-volatilization and found that it was reduced by application at 60 - 80°C. Steam volatilization could not account for the low application levels of 11 in this case, however, as a sealed system was used.

Organophosphorus insecticides have been observed to hydrolyse under dye-bath conditions [171, 172]. The hydrolysis rates of organophosphorus insecticides and their degradation products depend upon their chemical structure and in pH 6.0 buffered solutions at 70°C, half-lives range from 0.5 hours to 4.0 days [171]. These hydrolysis rates increase about four times for a temperature rise of 10°C [173]. However 11 was applied at 100°C for 0.5 hours at pH 4.5 from an aqueous emulsion. Under these weakly acidic conditions hydrolysis would not be expected to be significant for a phosphorothionate ester of the structure of 11 [173].

Recently Mayfield and Russell [80] found high losses of pyrethroid insecticides in the rinse liquors when the pyrethroids were applied to wool using 1% Teric N-13 as an application auxiliary. They concluded that this was probably associated with the cloud-point of the non-ionic surfactant which resulted in the deposition of the insecticide on the surface of the wool as the dye-bath was raised to the boil. Smaller losses were observed with other dyeing assistants. In other unpublished
work [174] losses of insecticide in rinse liquors have been found with most other non-polar insecticides; this has been found to be associated with the formulation and the particular insecticide.

In the present study, Teric N-13 had been used to prepare the aqueous emulsion of 11 and it is probable that a significant proportion of 11 was deposited on the surface of the wool as the temperature of the dye-bath passed the cloud-point. This surface application of 11 would be removed in the rinse liquor. For example, in one experiment, 32% of the applied 11 was found in the rinse liquors, 0.5% in the bath liquors and 66% on the wool giving a total recovery of 98.5%. This cloud-point effect is affected by other hydrophobic compounds in the emulsion as shown in Table 3.3.3.

<table>
<thead>
<tr>
<th>Ultraviolet Stabilizer (% o.f.w.)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HPLC method</td>
</tr>
<tr>
<td>0.05% Cyasorb UV 24</td>
<td>59</td>
</tr>
<tr>
<td>0.2% Cyasorb UV 24</td>
<td>62</td>
</tr>
<tr>
<td>0.8% Cyasorb UV 24</td>
<td>64</td>
</tr>
<tr>
<td>0.05% Tinuvin 320</td>
<td>54</td>
</tr>
<tr>
<td>0.2% Tinuvin 320</td>
<td>59</td>
</tr>
<tr>
<td>0.8% Tinuvin 320</td>
<td>50</td>
</tr>
<tr>
<td>0.2% Irganox 415</td>
<td>39</td>
</tr>
<tr>
<td>0.2% Benzophenone</td>
<td>53</td>
</tr>
<tr>
<td>0.2% 2,6-di-t-butyl-4-hydroxymethylphenol</td>
<td>69</td>
</tr>
<tr>
<td>0.2% Cyasorb UV 24 + 1% Lanasol red 5B dye</td>
<td>60</td>
</tr>
<tr>
<td>1% Lanasol red 5B dye</td>
<td>58</td>
</tr>
</tbody>
</table>

* 11 was applied to wool at 0.2% o.f.w.

To verify that poor recovery of the organophosphorus insecticide was due to poor application and not to poor extraction a total hydrolysis procedure was used. Treated wool was digested in KOH and the resulting
0,0-diethyl-phosphorothioic acid was alkylated to 0,0-diethyl-S-methylphosphorothiolate. This was determined by gas chromatography and confirmed (Table 3.3.3) that the extraction technique selected (5% HCl/dichloromethane-iso-octane (9:1)) removed at least 90% of 11 present on the wool.

3.3.4 PHOTODEGRADATION KINETICS

Although many workers have used first order kinetics for the degradation of pesticides on surfaces (based on empirical fitting of degradation curves) it has been claimed [175] that this concept has no basis in theory and that the disappearance of the pesticide was due to a variety of causes. Popendorf and Leffingwell [176] justified the first order kinetic model because, in addition to its empirical fit, it provides rate co-efficients and corresponding half-lives which permit a comparison between pesticides.

When wool containing known amounts of 11 was irradiated in the MBTF exposure box the loss of 11 could not be treated simply by first order kinetics, the rate of loss of 11 decreasing with time (Fig. 3.3.1). This was thought to be due to the combined effects of photodegradation and volatilization of 11 from the wool.

Even for apparently non-volatile insecticides, volatilization has been shown to be a major pathway for loss of insecticide from surfaces [177]. Pyrethroid insecticides used to mothproof wool follow a similar pattern to 11 [80]. It was thought that the insecticide on or near the wool surface was degraded more rapidly than insecticide that had penetrated the fibre and that the insecticide inside the fibre
Figure 3.3.1 Loss of $^{11}$ from wool

% $^{11}$ remaining

Exposure time (hr)
was only lost by volatilization or photodegradation at a significant rate after it had diffused to the surface of the fibre.

The losses of 11 due to volatilization were approximately determined by hanging treated wool samples on a 16 cm x 6 cm strip of aluminium 18 cm from the centre of a standard MBTF exposure box such that the aluminium strip shielded the wool sample from light. By simultaneously exposing a replicate sample to light the loss of 11 due to volatilization and photodegradation could be estimated.

As the rate of photodegradation is dependant on the light intensity reaching the target molecules and as the light intensity is dependant on the degree of transmittance of the light through the wool fibres and yarns, the rate of photodegradation of 11 would be dependent on its spatial location in the wool fabric and could not be described kinetically.

3.3.5 PHOTODEGRADATION PRODUCTS

In the solution photolysis of 11 the major photodegradation product found was the sulphoxide (44). However on wool an additional two products were detected. These were 4-ethylsulphinylphenol (41) and 4-ethylsulphonylphenol (42). After irradiation of wool initially containing 0.2 mg/g of 11 for 93 hours (in which time 47% of 11 was lost by photodegradation and 23% by volatilization) 0.022, 0.01 and 0.004 mg/g of compounds 44, 41 and 42 were recovered. In this case oxidation of the sulphide group to the sulphoxide was probably followed by further oxidation to the sulphone and/or aryl ester cleavage. Due to the volatility of 11 and its degradation products,
41, 42 and 44, it is impossible to determine with any accuracy the relative importance of the photodegradation pathways to these products.

Aryl ester cleavage has been reported previously [121, 123, 124, 160, 161] as a photochemical pathway for organophosphorus insecticide degradation but it would appear from the combination of results obtained in organic solutions and on the wool that the observed aryl ester cleavage in this case occurs via hydrolysis as it only occurs after prolonged exposure to light at 320°C in the presence of regain water on the wool. If aryl ester cleavage occurred via hydrolysis then, as in solution photolysis, the formation of the sulphoxide of II (44) was the major photodegradation reaction on wool (Fig. 3.3.2).

The non-appearance of the polar degradation product that was formed in polar solution may indicate that the majority of the insecticide was located in a non-polar environment inside the wool fibre or, alternatively, the polar product may not have been extracted from the wool.

3.3.6 EFFECT OF ULTRAVIOLET STABILIZERS ON THE RATE OF PHOTODEGRADATION OF O,O-DIETHYL-0-[4-ETHYLTHIOPHENYL]-PHOSPHOROTHIOATE

To compare the effect of the different UV stabilizers on the rate of photodegradation of II the residual insecticide after 93 hours irradiation was determined (Table 3.3.4).
Figure 3.3.2 Photodegradation pathways of 11 on wool.

\[
\begin{align*}
C_2H_5S\text{--}O-P\text{--}OC_2H_5 & \quad \text{(0.2 mg)} \\
11 & \quad \text{\downarrow} \\
& \quad \text{(UV) [0]} \\
C_2H_5S\text{--}O-P\text{--}OC_2H_5 & \quad \text{(0.022 mg)} \\
44 & \quad \text{\downarrow} \\
& \quad \text{(UV) [0]} \\
\left[ C_2H_5S\text{--}O-P\text{--}OC_2H_5 \right] & \quad \text{\downarrow} \quad \text{H}_2\text{O}^+ \\
42 & \quad \text{(0.004 mg)} \\
\end{align*}
\]
TABLE 3.3.4 Percentage of II Degraded on Wool After 93 Hours
Irradiation in Presence of UV Stabilizers

<table>
<thead>
<tr>
<th>Treatment (% o.f.w.)</th>
<th>1 Total loss (%)</th>
<th>2 Volatility loss (%)</th>
<th>1 - 2 Photodegradation loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05% Cyasorb UV 24</td>
<td>70</td>
<td>23</td>
<td>47</td>
</tr>
<tr>
<td>0.2% Cyasorb UV 24</td>
<td>65</td>
<td>25</td>
<td>40</td>
</tr>
<tr>
<td>0.8% Cyasorb UV 24</td>
<td>59</td>
<td>22</td>
<td>37</td>
</tr>
<tr>
<td>0.05% Tinuvin 320</td>
<td>57</td>
<td>21</td>
<td>39</td>
</tr>
<tr>
<td>0.2% Tinuvin 320</td>
<td>58</td>
<td>19</td>
<td>39</td>
</tr>
<tr>
<td>0.8% Tinuvin 320</td>
<td>54</td>
<td>21</td>
<td>47</td>
</tr>
<tr>
<td>0.2% Irganox 415</td>
<td>70</td>
<td>23</td>
<td>47</td>
</tr>
<tr>
<td>0.2% Benzophenone</td>
<td>68</td>
<td>21</td>
<td>47</td>
</tr>
<tr>
<td>0.2% 2,6-di-t-butyl -4-hydroxy- methylphenol</td>
<td>74</td>
<td>29</td>
<td>45</td>
</tr>
<tr>
<td>1% Lanasol Red 5B dye</td>
<td>49</td>
<td>21</td>
<td>28</td>
</tr>
<tr>
<td>1% Lanasol Red 5B dye + 0.2% Cyasorb UV 24</td>
<td>46</td>
<td>26</td>
<td>30</td>
</tr>
</tbody>
</table>

As in the case of the solution photolysis of II, of the ultraviolet stabilizers examined, Cyasorb UV 24 and Tinuvin 320 increased the light stability of II on wool to the greatest extent, but the protection obtained with these additives was only small. Significantly better protection was obtained with the fibre-reactive dye, Lanasol Red 5B, applied at normal levels (1% o.f.w.) used to dye wool and there was no additive effect when both the fibre-reactive dye (1% o.f.w.) and Cyasorb UV 24 (0.2% o.f.w.) were used. Dyestuffs have been shown to increase the durability of other types of insecticides on wool [178].

3.3.7 INSECTICIDAL ACTIVITY AGAINST TEXTILE PESTS

The insecticidal activity of II and its major photodegradation product, compound 44, is shown in Table 3.3.5. Both compounds displayed similar
activity and since 44 was stable to light, loss of insectproofness of wool treated with 11 after exposure to light at 320°C would be mainly due to losses of 11 and 44 by volatilization.

**TABLE 3.3.5 Insecticidal Activity of 11 and 44**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tineola bisselliella</th>
<th>Anthrenus flavipes</th>
<th>Tinea pellionella</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>44</td>
<td>0.005</td>
<td>0.005</td>
<td>0.01</td>
</tr>
</tbody>
</table>

For example when 11 was applied to wool to give a 0.01% uptake the fabric was initially insectproofed and only after exposure to light in excess of 100 hours did the feeding damage due to Tinea pellionella exceed 8 mg (Table 3.3.6).

**TABLE 3.3.6 Feeding Damage* (mg) Due to Tinea Pellionella**

<table>
<thead>
<tr>
<th>Exposure Time (hr)</th>
<th>Application level of 11 (% o.f.w.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
</tr>
<tr>
<td>50</td>
<td>5.9</td>
</tr>
<tr>
<td>97</td>
<td>6.8</td>
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<tr>
<td>150</td>
<td>16.4</td>
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<tr>
<td>220</td>
<td>12.5</td>
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<tr>
<td>290</td>
<td>10.2</td>
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<tr>
<td>360</td>
<td>14.8</td>
</tr>
<tr>
<td>455</td>
<td>11.7</td>
</tr>
<tr>
<td>550</td>
<td>15.2</td>
</tr>
</tbody>
</table>

* Wool is considered mothproof if feeding damage does not exceed 8 mg provided that controls exceed 30 mg.
At higher temperatures it would be expected that the loss due to
volatilization would be much greater.
4. CONCLUSIONS

The major photodegradation product of 0,0-diethyl-0-(4-ethyl-thiophenyl)phosphorothioate (11) in solution and on wool was 0,0-diethyl-0-(4-ethylsulphinylphenyl)phosphorothioate (44). In addition, on wool 4-ethylsulphinylphenol (41) and 4-ethylsulphonyl-phenol (42) were formed, probably as a result of hydrolysis by regain water on the wool.

2-hydroxybenzophenones and 2-hydroxybenzotriazoles with strong absorption in the solar ultraviolet region and with the ability to harmlessly transfer energy from the triplet state of an excited molecule were the most efficient type of ultraviolet stabilizers for compound 11 both in solution and on wool. However these ultraviolet absorbers were no more effective as ultraviolet stabilizers on wool than a fibre-reactive dye applied at normal levels.

Compound 44 was very stable photolytically and its insecticidal activity against tineola biselliella, anthrenus flavipes and tinea pellionella was similar to that of compound 11. These factors increase the apparent durability of 11 although loss of insectproofness of treated wool may occur by volatilization of 11 or 44. These compounds would also be expected to be readily removed by washing and drycleaning of the treated wool which would also result in loss of insectproofness. Recently the fastness properties of organophosphorus esters have been improved by attaching them to wool by covalent bonds [101]. The reasonable photostability of 11 and the excellent photostability of its major photodegradation product, 44, make 0,0-diethyl-0-(4-ethyl-
thiophenyl)phosphorothioate (11) an ideal structure from which to prepare fibre-reactive insectproofing agents.
## APPENDIX

PROGRAM FOR CALCULATION OF HALF-LIVES AND THEIR CORRELATION CO-EFFICIENTS
FOR 0,0-DIETHYL-O-(4-ETHYLTHIOPHENYL)PHOSPHOROTHIOATE.

<table>
<thead>
<tr>
<th>000</th>
<th>76 LBL</th>
<th>048</th>
<th>00</th>
<th>0</th>
<th>096</th>
<th>02</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>16 H*</td>
<td>049</td>
<td>05</td>
<td>5</td>
<td>097</td>
<td>03</td>
<td>3</td>
</tr>
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<td>002</td>
<td>25 CLR</td>
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<td>06</td>
<td>6</td>
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<td>01</td>
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<td>051</td>
<td>69</td>
<td>DP</td>
<td>099</td>
<td>07</td>
<td>7</td>
</tr>
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<td>00 OQ</td>
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<td>04</td>
<td>O4</td>
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<td>02</td>
<td>2</td>
</tr>
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<td>005</td>
<td>03 3</td>
<td>053</td>
<td>69</td>
<td>DP</td>
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<td>06 6</td>
<td>054</td>
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<td>05</td>
<td>102</td>
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<td>055</td>
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<td>03</td>
</tr>
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</tr>
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