AN ABSTRACT OF THE THESIS OF

Edmund Moses Nso Ndip for the degree of Master of Science

in Chemistry (Organic) presented on December 18, 1981

Title: THE PHOTOCHEMICAL TRANSFORMATION OF OXIME CARBAMATES

Abstract approved: Redacted for privacy

Dr. Peter K. Freeman

The photolysis of aldicarb (7) (CH_3CN, 254 nm) yields a number of products but more significantly: methylamine, dimethylamine, dimethyl-disulfide, tetramethylsuccinonitrile and 1-methyl-2,3-dicyano-2,3-dimethylbutane. The same array of products is obtained when aldicarb is photolysid in the presence of sensitizers (benzophenone, benzonitrile, and acetophenone). These results suggest that the triplet excited state is the product forming intermediate.

On the other hand, the irradiation of methomyl (8) (THF, 254 nm) gives methylamine, acetonitrile, dimethylamine, dimethyl disulfide, the methylhydrazone of biacetyl and carbon dioxide. When photolysed in the presence of sensitizers (benzophenone, benzonitrile and acetophenone) the same array of products is obtained in approximately higher yields.

The photochemical transformation of oxime carbamates proceeds to products through the triplet excited state.

The Photochemical Transformation of Oxime Carbamates

by

Edmund Moses Nso Ndip

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Typed by Jo Ann Linch for Edmund Moses Nso Ndip

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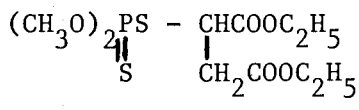
THE PHOTOCHEMICAL TRANSFORMATION OF OXIME CARBAMATES

INTRODUCTION

Insecticidal compounds interfere specifically with some vital components of life processes of certain organisms (1). While these substances have been used to achieve desired beneficial effects, unwanted effects resulting from their application in the environment have presented serious problems. Members of an important subgroup are capable of photoinduced reactions often yielding products more toxic than the parent compound (2). This increased toxicity has been observed in mammals and some fish (3).

Each year billions of pounds of insecticides are used for one reason or the other (4). Only recently, July, 1981, about 130,000 square miles of farmland in California were sprayed with Malathion, an organophosphorus insecticide, because of an outbreak of vegetable and fruit infestation by the Mediterranean fruit fly, Ceratitis Capitata. One of the fears was that , it, like many other insecticidal compounds might be capable of inducing undesirable side effects in humans.



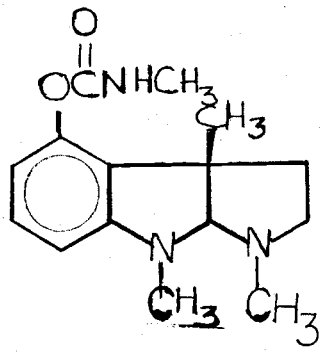
(1)

The metabolism of insecticidal compounds including carbamates has been the subject of many studies and publications. On the other

hand, their photochemistry remains relatively unknown. Their metabolism often yields persistent compounds. Whether their photo-induced reactions are capable of such behaviour will not be known until after their photochemistry is studied. Thus, such a photochemical study should be able to provide information about the products obtained, how they are formed, and how much of each is formed. It should also be possible to obtain information about the product determining intermediate. In order to carry out this study, it is essential that related aspects of carbamate chemistry, metabolism, toxicology and other available information be reviewed.

Historical Development

The use of plant seeds or beans as a means of proving guilt is nothing new to most native West Africans. Even small green peppers have been used for this purpose by the Bayangs of Cameroon. The use of beans from physostigmine venenosum is common among the Calabarians of Nigeria (5). It was not until 1864 that the active compound, eserine (2) was isolated and its properties studied (6).



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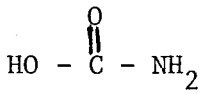
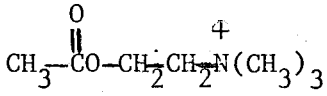
Stedman and Barger established the structure of eserine (2) in 1925 (7). It can be seen that eserine is a derivative of carbamic acid (3). The



(3)

basis for its pharmacological properties had to await the discovery of acetylcholine (4) as a neurotransmitter substance, and the role of cholinesterase in degrading acetylcholine. The blocking action of eserine on cholinesterase was shown by Engelhart and Loewi in 1930 (8). Since then, a number of synthetic analogs such as prostigmine (5) have been studied.



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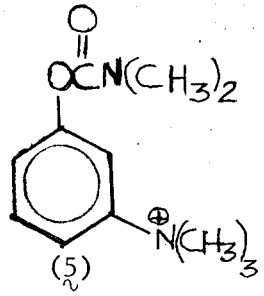
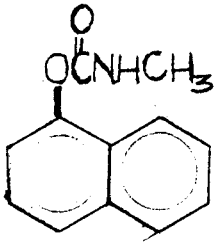


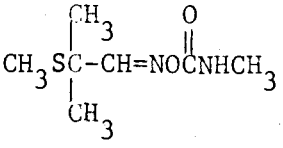
(5)

Unfortunately, "medicinal carbamates" as they are called are quite strong bases and hence are ionizable in aqueous solutions. Consequently, they have very low lipid solubility; and hence, they are unable to penetrate the ion-permeable sheath which surrounds the insect nervous system. It is probably for this reason that they are not harmful or capable of poisoning insects. The first insecticidal carbamates were made by the Geigy Company of Switzerland in 1947. They were all N,N-dimethylcarbamates. It was not until later that it was discovered N-methylcarbamates constitute an even more potent

group. The first of the insecticidal N-methylcarbamates, Sevin (6) was discovered and described in 1957 (9); while the oxime carbamate aldicarb (UC 21149) (7) was described in 1965 (10). Since then the number of insecticidal oxime carbamates has increased. Methomyl (8) was introduced in 1967 by E. I. duPont de Nemours as an experimental insecticide-nematicide under the trade name Lannate. It has registration for foliar applications for a variety of fruit and vegetable crops. Methomyl is classified as a systemic insecticide and acaride (11).



(6)



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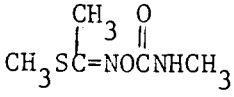
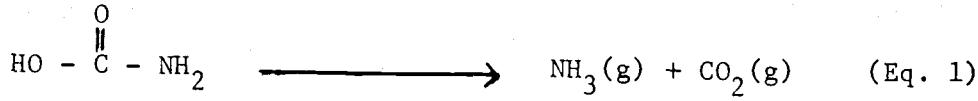


(8)

Synthetic and Related Chemistry of Carbamates

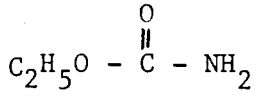
The backbone of all carbamates is carbamic acid (3). Its salts are more stable whereas the acid in the free form quickly decomposes into ammonia and carbon dioxide (Eq. 1). Formation of an alkyl or



(Eq. 1)

aryl ester provides a stable carbamate species. The formation of ethylcarbamate or urethane (9) is an example. Urethanes have found

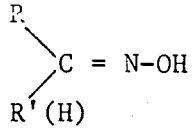
a wide variety of uses in commerce (12). Unfortunately, certain



(9)

analogs of urethane are carcinogenic to lungs and other mammalian tissues (13).

One class of methylcarbamate insecticides is derived from aliphatic oximes (10). When these substrates are coupled with methylcarbamic acid, insect poisons with general structure (11) result. In addition to (7) and (8) other examples are thiocarboxime (12) and oxamyl (13).



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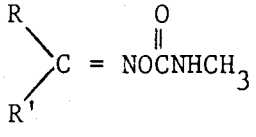

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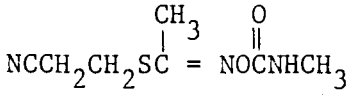

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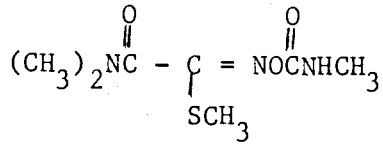


(13)

They are usually slightly white odorous crystalline solids with high melting points and low vapour pressures. They decompose slowly in aqueous solutions. They dissolve readily in most organic solvents but are only slightly soluble in water excepting aldicarb and methomyl.

On application to environmental surfaces, certain methylcarbamates are susceptible to atmospheric oxidation and photochemical decomposition. On heating, they give methylisocyanate and the parent hydroxy species (Eq. 2).

$$ROCNHCH_3 \xrightarrow{\Delta} ROH + CH_3N = C = O \quad \text{(Eq. 2)}$$

Base hydrolysis has been of considerable interest. Some dependence on the chemical structure of the insecticide has been studied and several mechanisms have been proposed (14,15).

The methods used in the synthesis of oxime carbamates or esters of carbamic acid usually involve one or two-step reactions. The following general reactions (Eq. 3, 4, 5) have been employed (16-21):

$$ROH + COCl_2 \longrightarrow ROCCl \xrightarrow{CH_3NHCH_3} ROCN(CH_3)_2 \quad \text{(Eq. 3)}$$

$$RONa + ClCON(CH_3)_2 \longrightarrow ROCN(CH_3)_2 \quad \text{(Eq. 4)}$$

$$ROH + OCNCH_3 \longrightarrow ROCNHCH_3 \quad \text{(Eq. 5)}$$

However caution must be exercised with oximes as their intermediate chloroformates rapidly decompose to the corresponding nitriles at above ambient temperatures (Figure 1) (23).

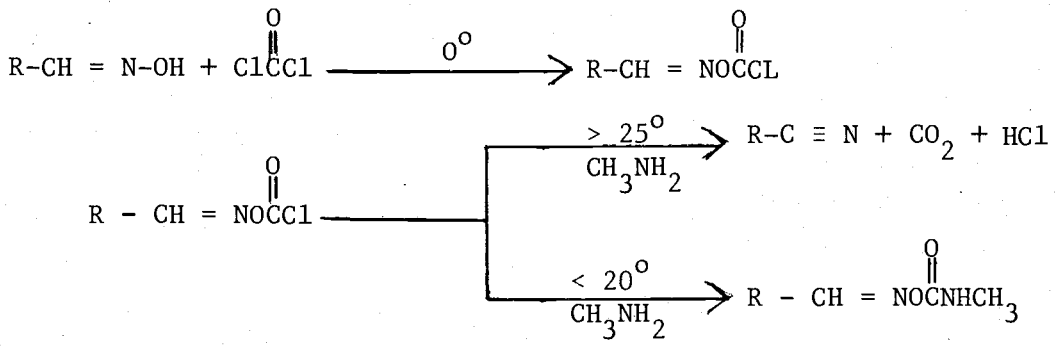
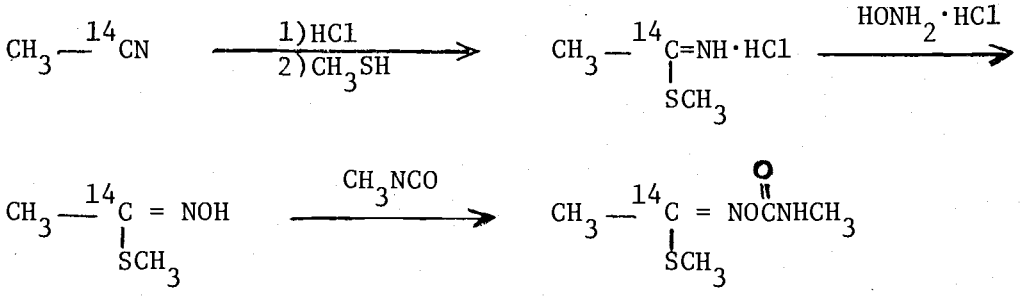


Figure 1. Reaction of oxime chloroformates with methylamine at different temperatures.

Besides the patented methods, aldicarb and methomyl have been synthesized by a number of workers. Bartley (24) and Harvey et al (25) have synthesized isotopically labelled aldicarb and methomyl respectively; a three-step reaction sequence was used to synthesize methomyl starting from C-14 labelled acetonitrile. The following reaction sequence was used:



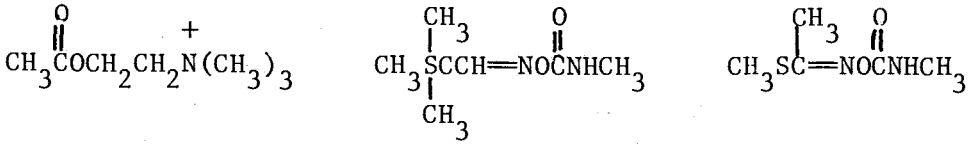
Other synthetic methods can be found in the literature (26-30). In addition to the synthesis of parent compounds, a number of metabolites

have also been synthesized. Insecticide isotipic-tagging for degradative pathway definition is a critical part of the EPA registration process (22).

The common degradation reactions involving carbamates include hydrolysis, oxidation and conjugation. Hydrolysis gives parent hydroxy compounds (phenols, naphthols, enols, etc.) plus methylamine and carbon dioxide (22).

Insecticidal Activity and Mode of Action of Carbamates

The toxic carbamates are fairly potent inhibitors of cholinesterase with cholinergic symptoms on "intact animals". Insecticidal carbamates are also known to be acetylcholinesterase inhibitors. It is said that there seems to be a direct link between enzyme inhibition and toxicity. A look at the structure of acetylcholine (4), aldicarb (7), and methomyl (8) shows a comparison that could be used to deduce an activity-structure relationship (31). It should be noted that aldicarb arose from synthetic attempts to emulate acetylcholine.



(4) (7) (8)

Figure 2. Structure of acetylcholine (4), aldicarb (7), and methomyl (8).

How does enzyme inhibition occur? Acetylcholinesterase (AChE) hydrolyses acetylcholine (ACh) to acetic acid and an aminoalcohol

(choline) as shown in Figure 3 (22). Carbamate insecticides also react with acetylcholinesterase according to the following sequence of equations (22) (Figure 4):

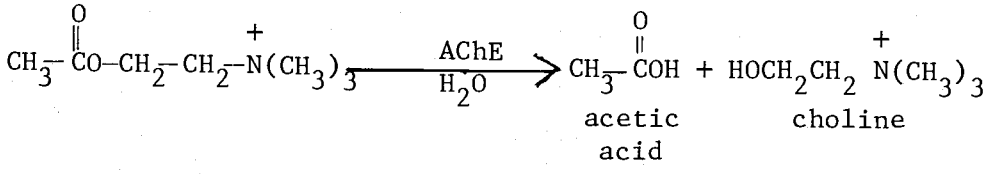


Figure 3. Hydrolysis of acetylcholine by acetylcholinesterase.

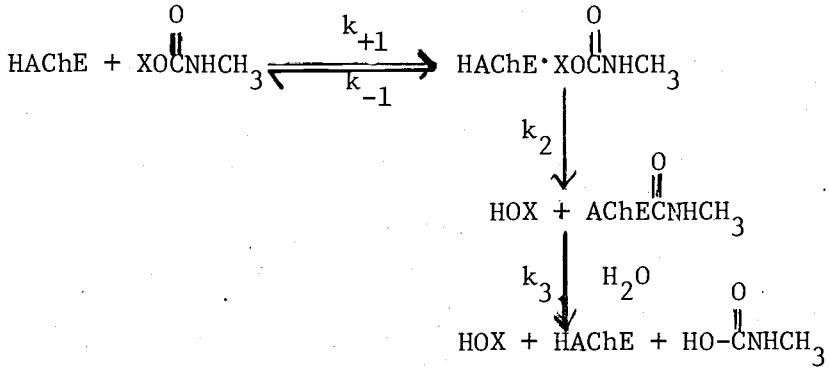


Figure 4. Reaction of carbamate insecticides with acetylcholinesterase.

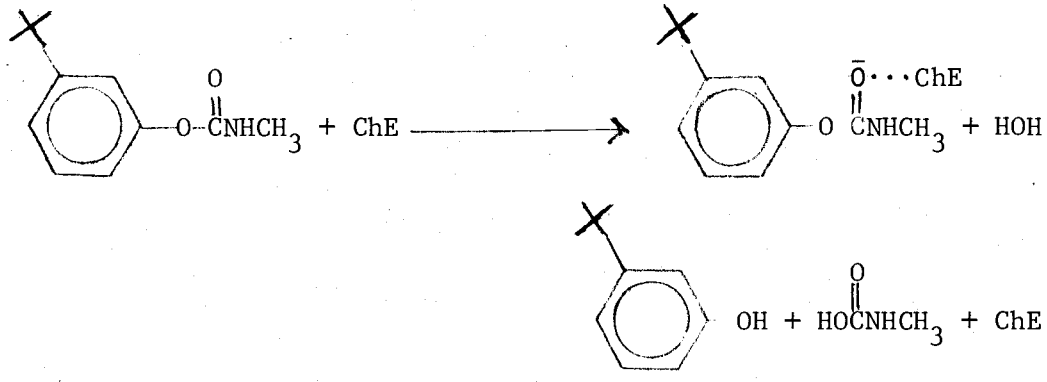


Figure 5. Reaction of physostigmine with cholinesterase (32).

The exact biochemical mechanism for the inhibition seems to be known and acetylcholinesterase is the enzyme of importance with respect

to carbamate poisoning. Other cholinesterases would react in the same manner. The reaction begins with the enzyme HAChE coupling with the insecticide to form an intermediate complex (k_{+1}) which may then dissociate to enzyme and carbamate (k_{-1}) or decompose to a stable carbamylated enzyme plus a leaving group (k_2). The leaving group varies depending on the parent methylcarbamate. The carbamylated enzyme is then hydrolyzed generating the free enzyme and methylcarbamic acid (k_3). No destruction of acetylcholinesterase is achieved. Within a nerve synapse, AChE cleaves the transmitter. When an insecticidal carbamate enters the synapse during poisoning, it "competes" with ACh for the active site on the enzyme. If successful, it ties up the enzyme allowing poisoning to occur. Therefore, the more enzyme tied up, the more severe the poisoning.

Independent structure-activity studies indicate a dependence on size, shape and electronic properties of oxime substituents of enzyme inhibition. It is probably for this reason that aldicarb is assigned the E configuration (33). Kohn et al. (1965) determined such dependence for simple alkyl phenyl carbamates (34). Whether a particular configuration has been assigned to methomyl (8) is not known. Additional discussions on structure-activity relationship can be found in the literature (35-40).

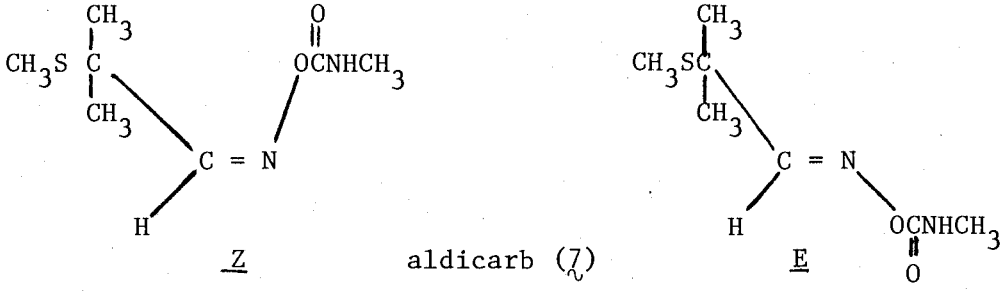
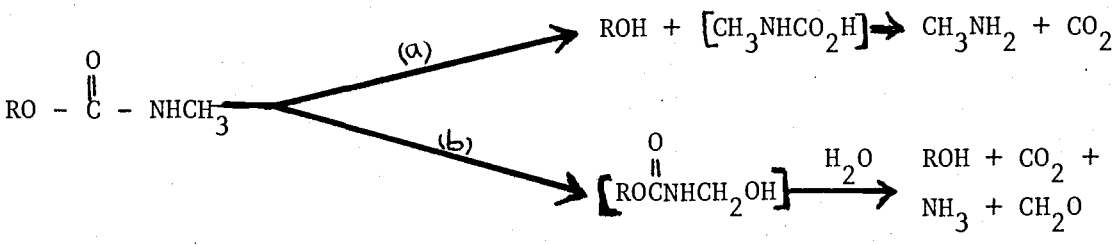


Figure 6. Stereoisomers of aldicarb.

Methomyl has residue tolerances of 10 ppm for forage and ranges from 0.1 to 6.0 ppm for food crops. Residual persistence is short, with a half-life of less than a week on most plant foliage. A large number of pests are controlled by the insecticide including alfalfa weevil, various aphids, codling moth, corn earworm, diamond black moth, European corn borer, tobacco horn worm and others. It is virtually non-toxic to mammals when applied dermally as a water slurry (more than 5000 mg per kg. LD_{50} for rabbits), but its low rat oral LD_{50} of 21 mg per kg requires that care be taken when applied.

Metabolism of selected carbamates

Metabolism seems to be the most widely studied aspect of carbamate biochemistry. Carbamates are metabolized by two basic mechanisms, both involving breakage of the carbamate ester linkage, namely by direct esterase attack (path a), or by initial oxidation by mixed-function oxidases (MFO) followed by hydrolytic breakdown of an unstable intermediate (path b) (41a).



The metabolism of Carbaryl has been extensively studied in insects and mammals and a scheme showing the metabolic pathways has been proposed (41b). The complete metabolism of aldicarb (7) in cotton plants was observed to occur in less than two days by Bull (41c). The sulfoxide

seems to be the primary metabolite. Metcalf noted that the sulfoxide was the more active cholinesterase inhibitor and not the parent aldicarb (42). Bartley et al. (1970) (43) performed the most extensive work on aldicarb metabolism noting two pathways: hydrolysis to the oxime or oxime sulfoxide and oxidation to aldicarb sulfoxide and sulfone (Figure 7). Aldicarb nitrile metabolites include (9) and (10).

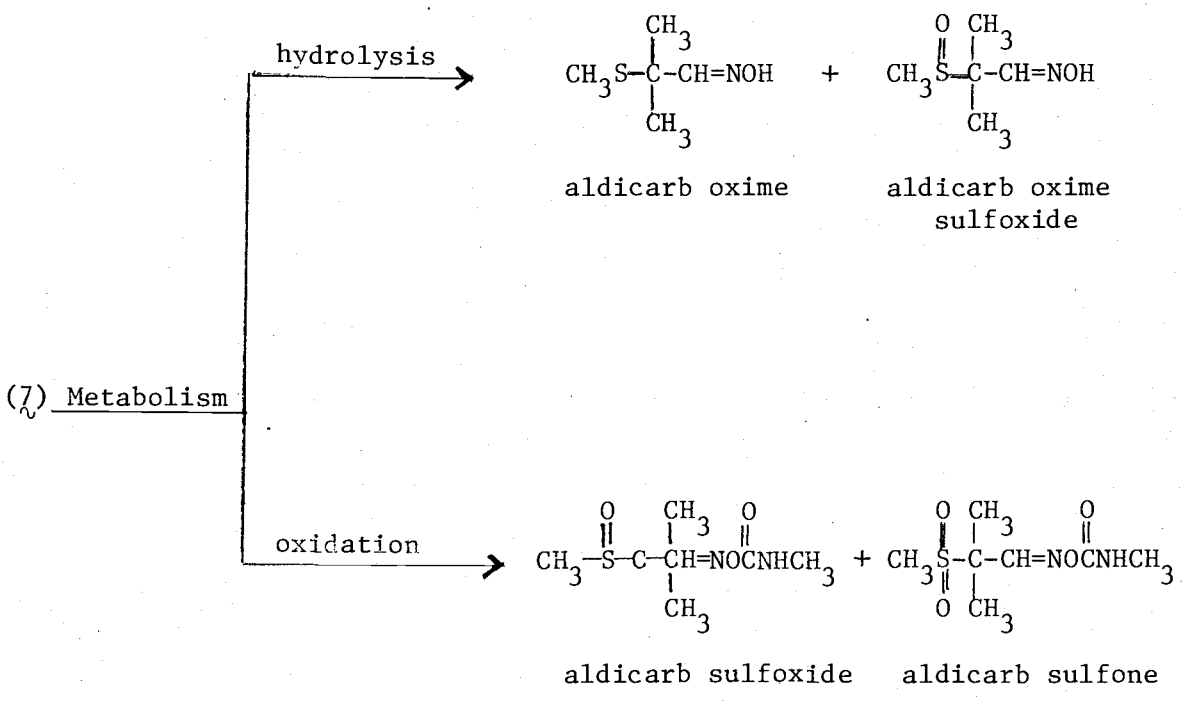
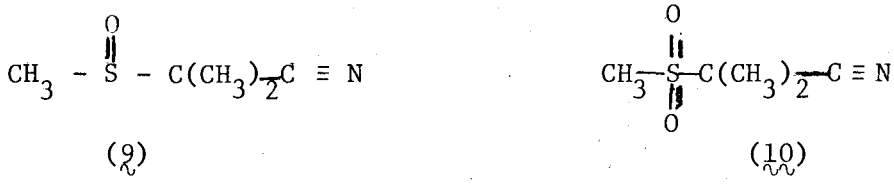


Figure 7. Metabolism of aldicarb.



(9) (10)

While the metabolism of aldicarb gives rather large chemical fragments, the metabolism of methomyl often yields simple chemical fragments (44, 45). The pathway involves the degradation of isotopically labelled methomyl to ^{14}C-carbon dioxide and ^{14}C-acetonitrile (22).

$$CH_3S-\overset{CH_3}{\overset{|}{\underset{}{{}^{14}C}}}=NOC(=O)NHCH_3 \longrightarrow {}^{14}CO_2 + CH_3-{}^{14}CN \qquad \text{(Eq. 9)}$$

Figure 8. General metabolic pathway of methomyl proposed for animals and plants.

The hydrolysis product of methomyl, S-methyl-N-hydroxy thioacetamidate, the sulfoxide and sulfone of methomyl were not detected as metabolites. This degradative pathway is even simpler for metabolism in soils with ^{14}C-carbon dioxide being the only significantly labelled metabolite formed. In rats most of the radioactivity is recovered in exhaled air (Figure 9).

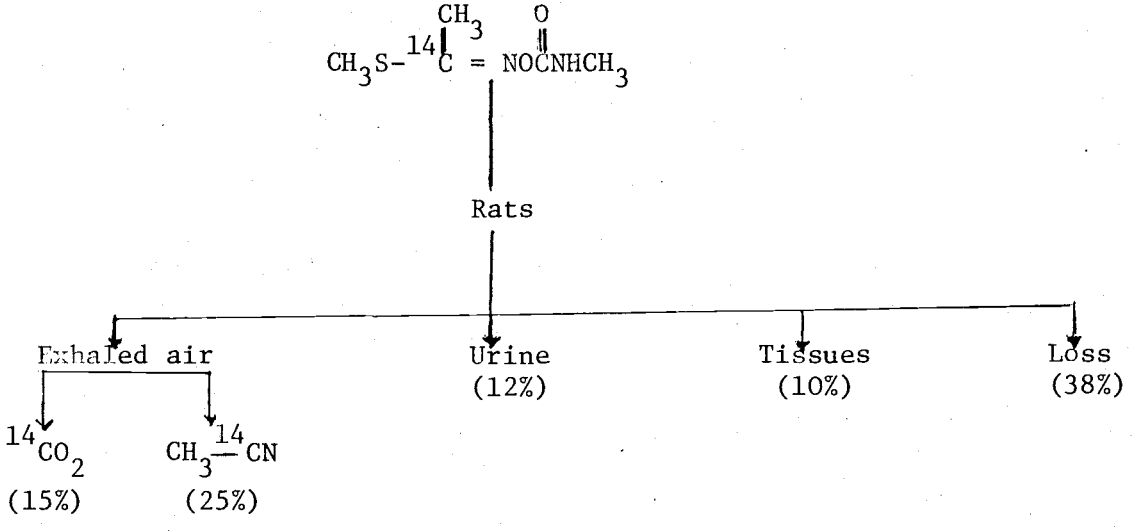


Figure 9. Disposition of methomyl (percent of dose) 24 hours after oral treatment of rats (44).

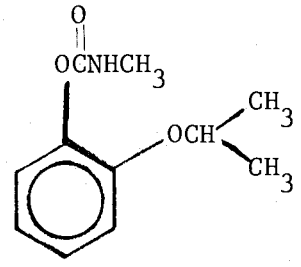
While aldicarb is seen to give significantly persistent metabolites, methomyl does not. Consequently, only the parent compound is to be watched following application.

Analysis of Selected Carbamates

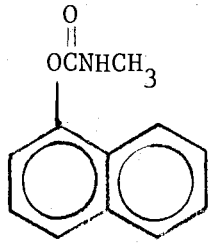
A great many methods have been developed for both quantitative and qualitative analysis of insecticidal carbamates. Such methods include colorimetry, enzymatic analysis, fluorescence, gas chromatography and thin-layer chromatography (22). The method used often depends on the properties of the carbamate. Each method employed is not without its problem. Even with these problems, the discovery of specific detectors makes gas chromatography the more versatile and most used method. Most insecticidal methylcarbamates are thermally unstable and are often retained in column supports during analysis. In addition, most insecticidal carbamates do not respond to electron capture but partial solutions have been obtained (46-48). Sulphur-containing carbamates have been analyzed using nitrogen-specific detectors and flame photometric detectors (49).

Using conventional GLC parameters, (Baygon, Zectran, and Matacil) give responses equivalent to 90% of the injected compound when an OV-17 column is operated at 180°C (50). Carbaryl shows slight decomposition on a DC-200 column at 180° (51). Column support deactivation is a suggested means of easing the determination of thermally unstable compounds. Carbaryl, Mesurol and Zectran were recovered intact in yields greater than 90% when acid-washed chromosorb W coated with 6% carbowax 20M is heated to 260-280° overnight and

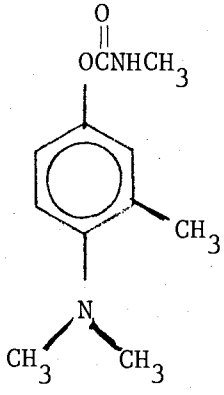
extracted exhaustively with methanol (52). Methomyl residues in water, soils, sediments and tobacco have been determined on a 10% DC-200 column at 140° using a flame photometric detector (53). Also methomyl seems to chromatograph well when injected into a 6% OV-210/4% OV-101 mixed phase column at 160°C (54). Leitch used a microcoulometric detector (55). FFAP columns have been used with great success (56).



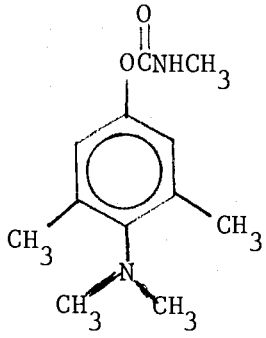
Baygon



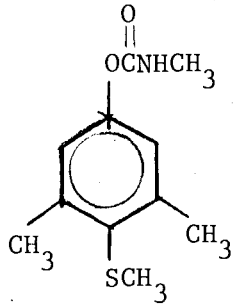
Carbaryl



Matacil



Zectran



Mesurol

Figure 10: Structure of some analyzed carbamates.

In our laboratory, methomyl has been chromatographed successfully using a 20% Carbowax 20M aluminium column on Chromosorb W AW DMCS 80/100 mesh at 70°C and in a separate analysis using a 10% Dinonyl phthalate column on Chromosorb W AW DMCS 60/80 mesh at 55°C. The reproducibility was good but the recovery level is low. Several methods have been used to chromatograph aldicarb (57).

Photochemistry of Oximes and Related Substrates

Insecticidal oxime carbamates are multi-functional substrates as can be seen from the general structure (11). It is thus not surprising to find that the photochemistry of oxime carbamates could possibly be understood in terms of the photochemistry of composing functionalities. If oxime carbamates are reduced to the general formula $RO\overset{O}{\overset{\|}{C}}NHR'$, then they could be considered as esters, amides, oximes and sulfides when substitution in the R group is considered.

Three cleavage patterns are observed when an ester is irradiated (Figure 11) (58).

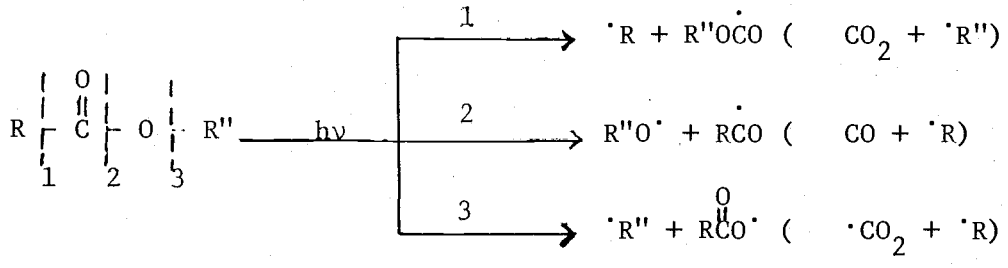
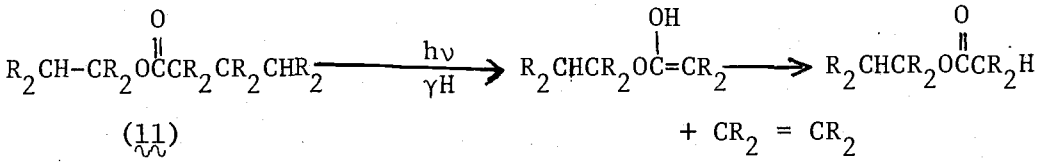


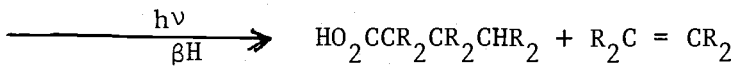
Figure 11. Cleavage patterns in esters.

The R-group could be a hydrogen or an alkyl group. The radicals obtained could undergo further reactions. Reactions analogous to

"Norrish Type II" splits of aldehydes and ketones could be observed depending on the position of the hydrogen atom (β or γ).



(11)



Irradiation of an amide results in two cleavage patterns with the dominant process being generation of free radicals by carbon-carbon and/or carbon-nitrogen cleavage next to the carbonyl. Higher amides show "Norrish Type II" cleavage (Eq. 9), while simpler amides give nitriles as a result of photochemical dehydration (Eq. 10) (59).

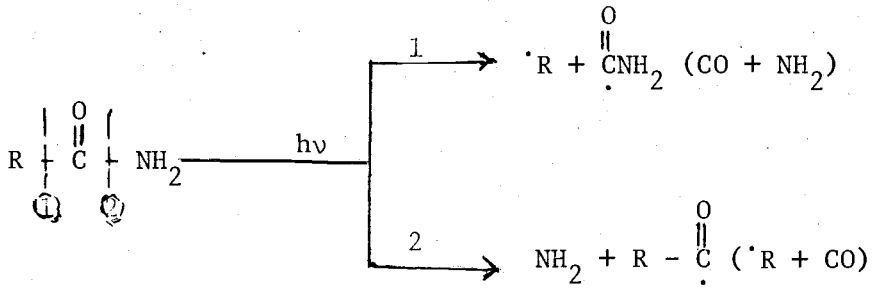
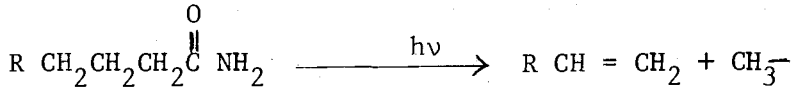


Figure 12. Cleavage patterns in amides.



(Eq. 9)

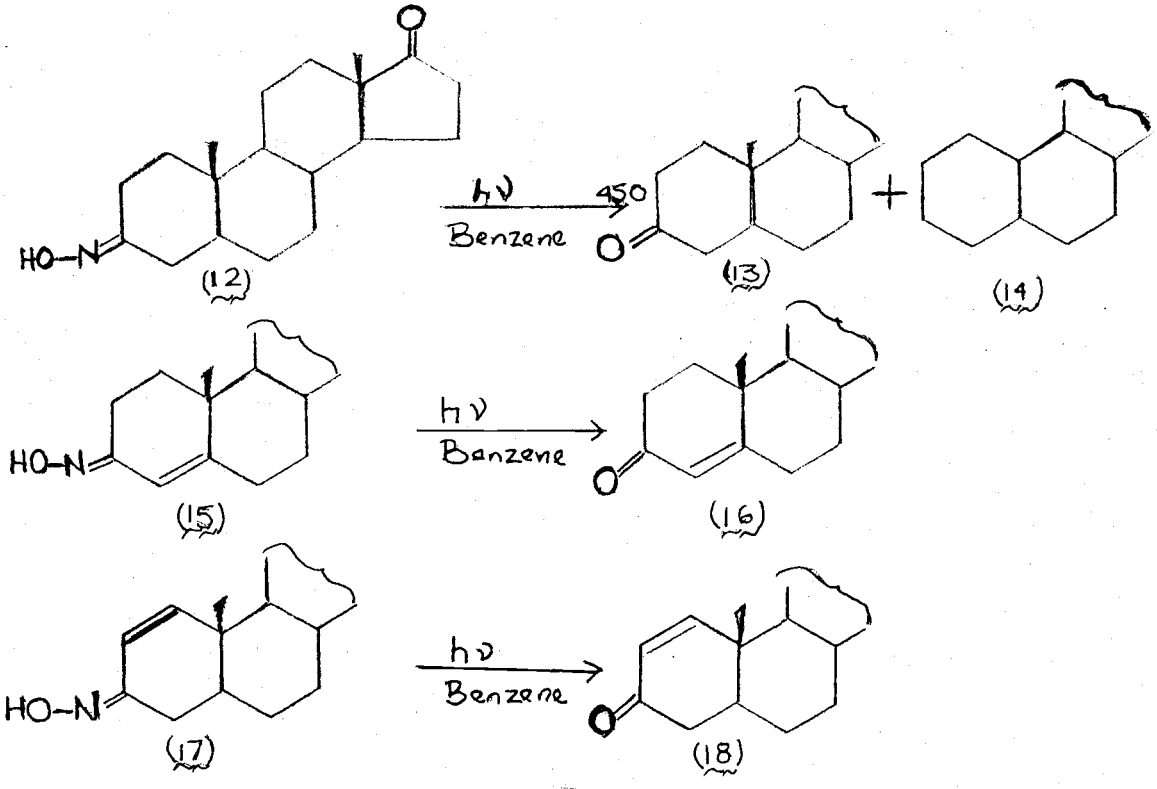
(Eq. 10)

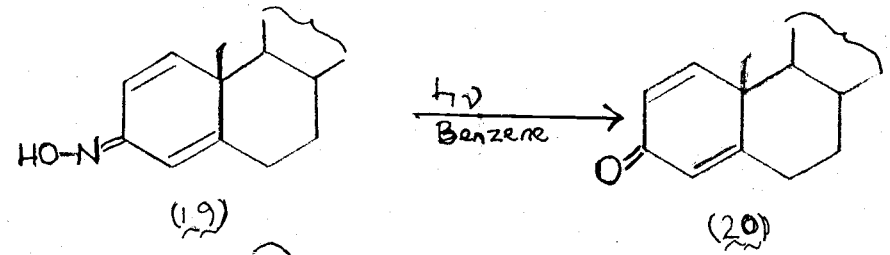
A sulfide linkage is present in insecticidal oxime carbamates. Sulfides yield abstracting radicals capable of recombination (60). Significantly sulfides and disulfides react photochemically according to Eq. 11 and 12.

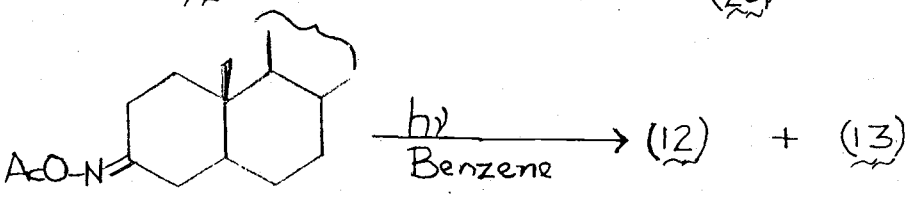
$$R\text{-}S\text{-}R \xrightarrow{h\nu} RS^{\cdot} + {}^{\cdot}R \qquad \text{(Eq. 11)}$$

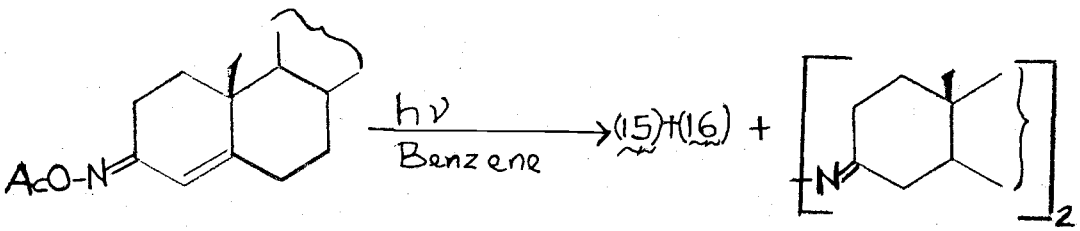
$$R\text{-}S\text{-}S\text{-}R \xrightarrow{h\nu} 2\ RS^{\cdot} \qquad \text{(Eq. 12)}$$

Irradiation of an oxime yields through a variety of reactions a variety of products. Oximes are known to undergo the photochemical Beckmann rearrangement to amides, hydrolysis to ketones and Z-E isomerization (61-67). Vermes and Beugelmans studies the photochemistry of oximes and acetates of a series of steroids (68) (Eq. 13-18) in 0.5% solutions in benzene.

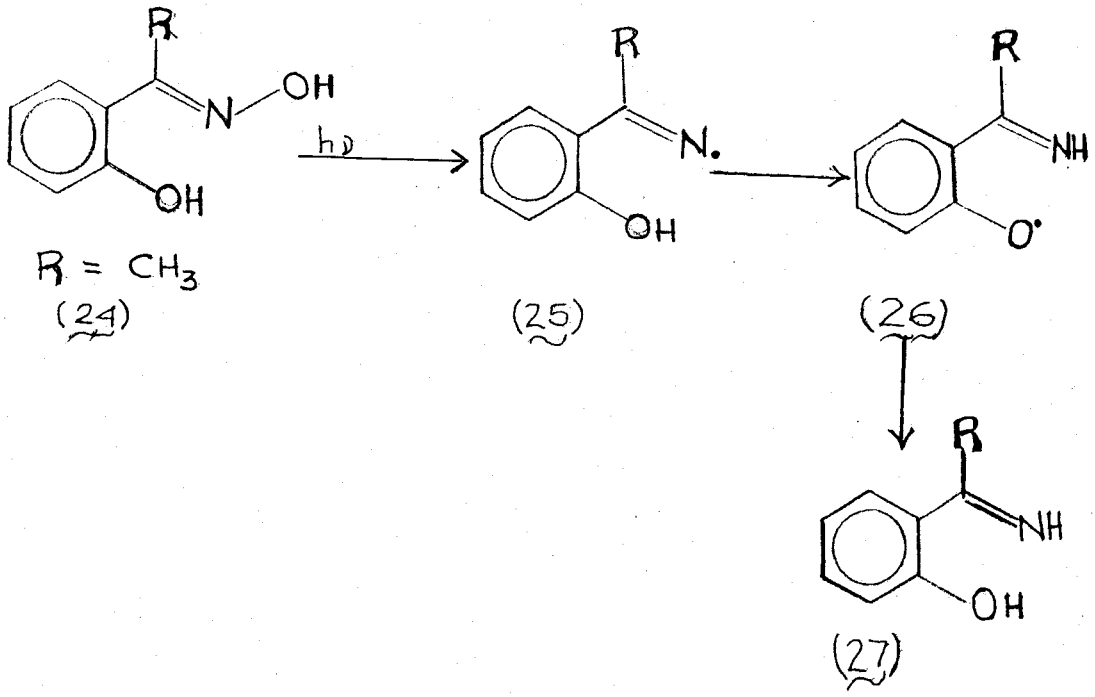




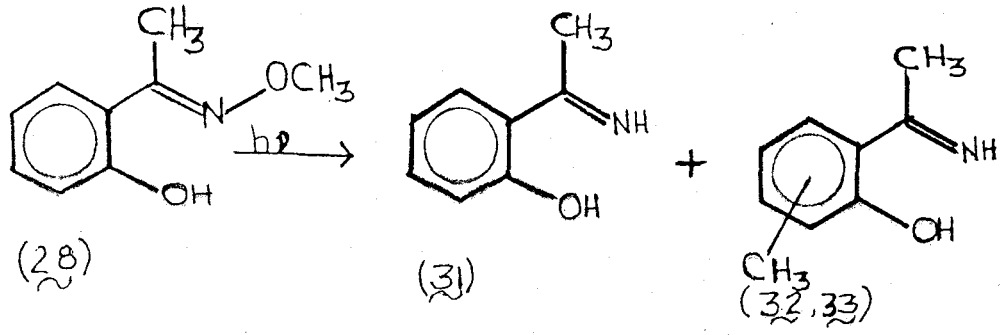


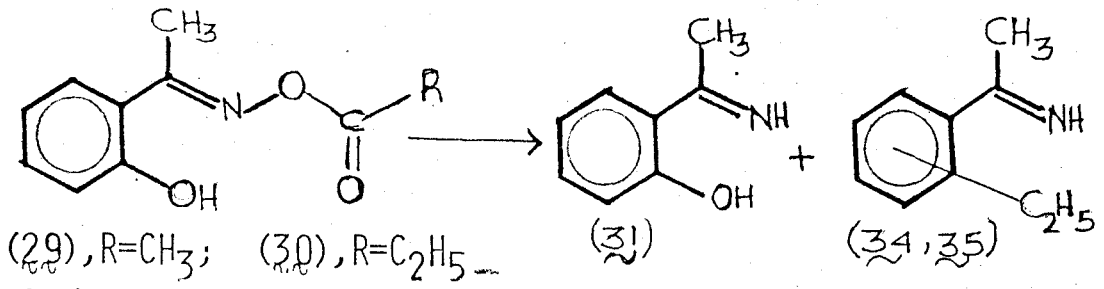


Vermes and Beugelmans observed mostly the formation of ketones and oximes. On the other hand, when Grellmann and Bauer (1974) studied the photochemistry of aromatic ketoximes (69), they observed mostly ketimines.

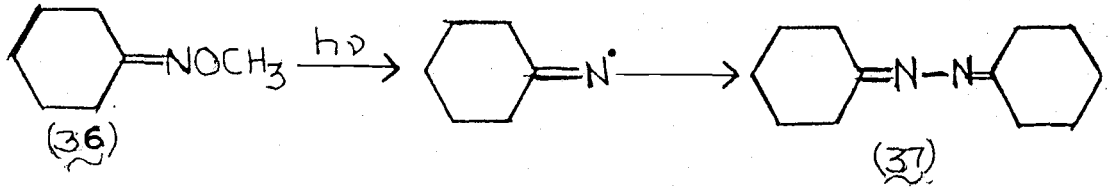


Okada et al. (1969) studying acetophenone oxime esters observed no dimerization of (25) when there is no O-hydroxy group (70). Additional products are obtained when the oxime ether (28) and oxime esters (29, 30) are irradiated.





The ketimines once formed can be hydrolysed to give ketones. Derivatives containing a nitrogen-nitrogen bond instead of a nitrogen-oxygen bond do not form ketimines. Azine formation was observed by Vermes (23) and by Sato (1972), who obtained (37) on irradiating O-methylcyclohexanone oxime (36) (71).



The formation of (37) is explained by an initial nitrogen-oxygen homolytic cleavage forming the iminyl radical followed by radical

recombination. This sequence of events is echoed by the work of Ishikawa et al. (1975). They studied the photochemical decomposition of O-acyl oximes (72). The radicals which are formed as a result of homolytic nitrogen-oxygen bond fission combine with solvent to give products. The fact that carbon dioxide is obtained suggests that no other bond fissions occur initially (Figure 13).

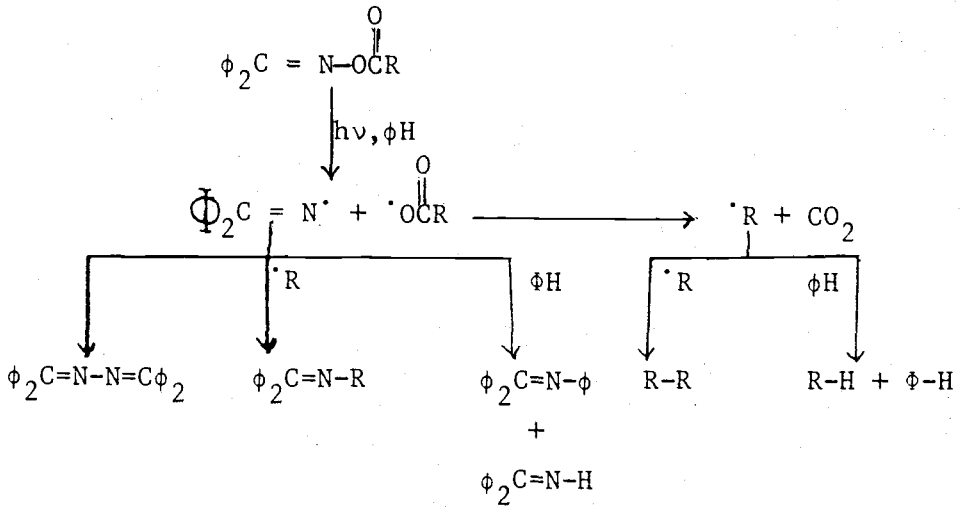
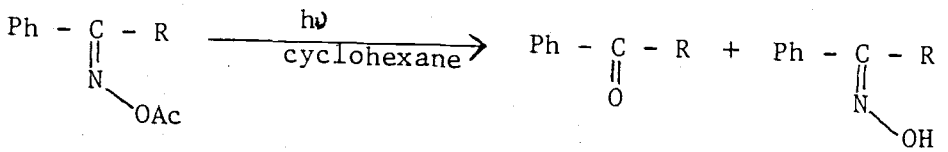


Figure 13. Photochemical decomposition of O-acyl oximes.

Independent studies on the mechanism of the photochemical Beckmann rearrangement have been carried out by Oline in 1969 (66) and Beugelmans in 1971 (73). It was proposed that the rearrangement proceeds through an oxaziridine intermediate. Beugelmans et al. studied the process illustrated in Eq. 19. According to Beugelmans et al.

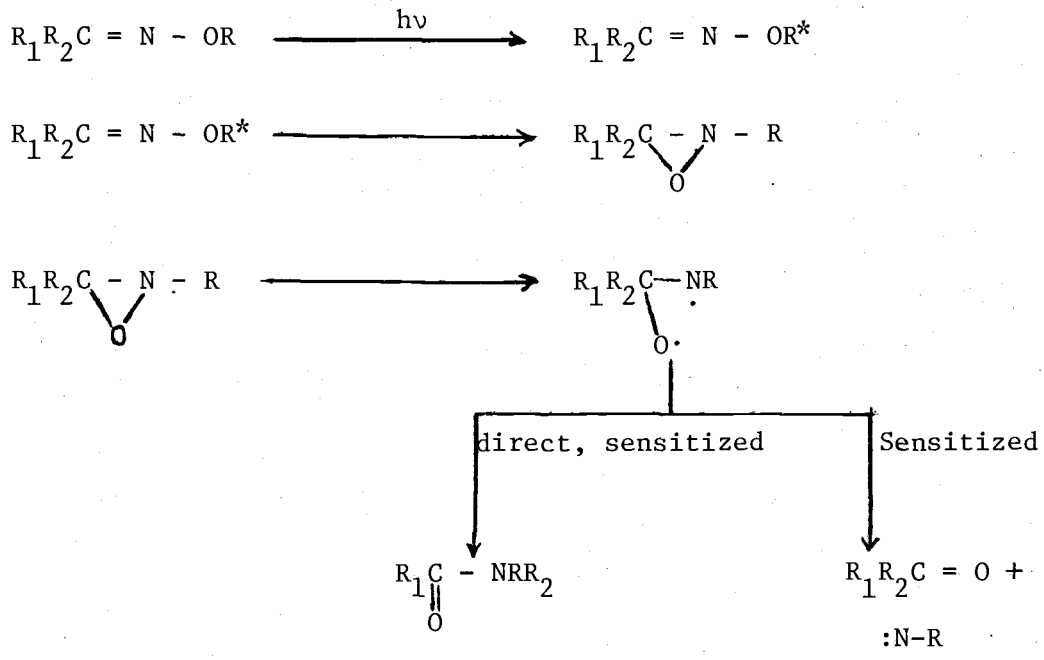


(Eq. 19)

(38), R = CH_3 (39), R = CH_3 (40), R = CH_3

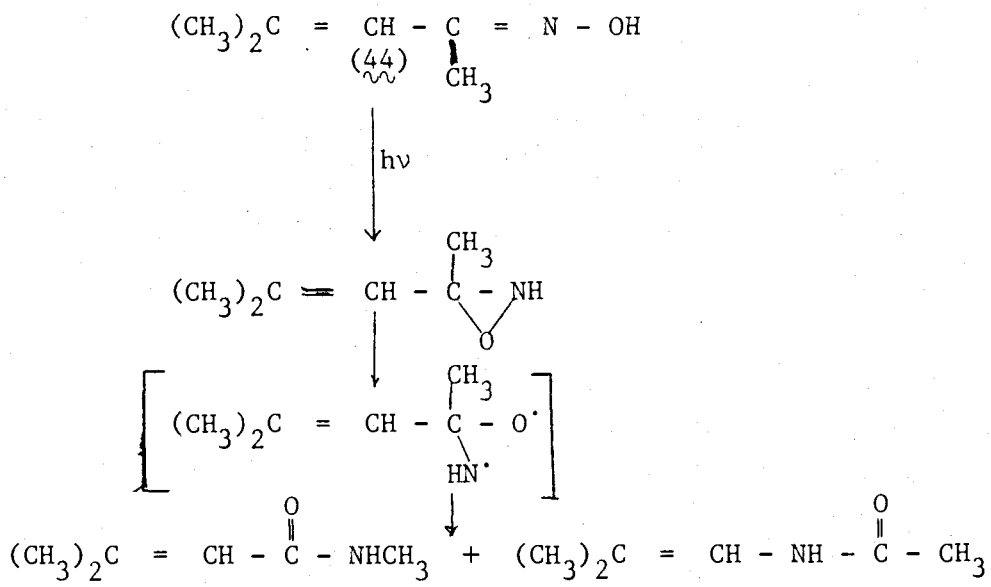
(41), R = Ph (42), R = Ph (43), R = Ph

the oxaziridine intermediate formed cleaves homolytically to form a diradical which then rearranges to form products. In the direct irradiation the reaction is believed to proceed through a singlet excited state to form the amide. In a photosensitized reaction a ketone and an amide are formed. Oxime formation is the result of homolytic cleavage of the O-acyl bond to give the iminoxy radical C=N-O· which then picks up a hydrogen atom from the solvent.

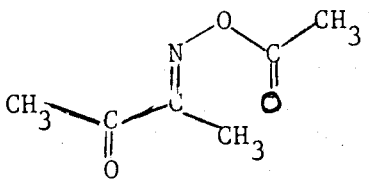


A similar mechanism was used to explain the results of the irradiation of mesityl oxide oxime (44) by Sato.

Baas and Cerfontain in a number of studies on α-Oxo Oximes from 1977 to 1979 have obtained a diverse number of products from a combination of processes including photoisomerization, photochemical Beckmann



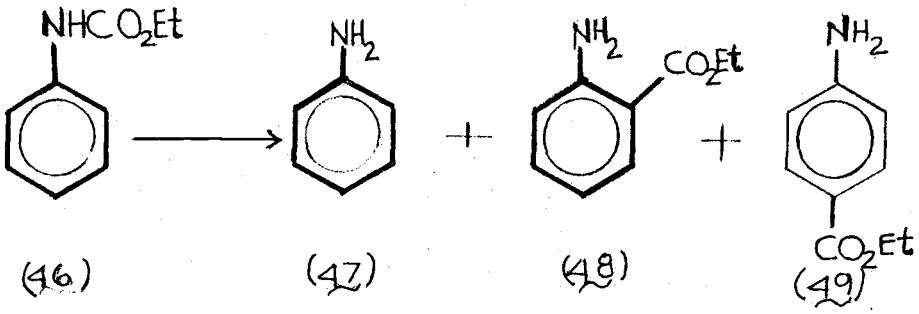
rearrangement, decomposition and radical recombinations. On irradiating an α-oxo-oxime (45) 17 products were obtained (74). The photodecomposition of (45) occurs via two pathways:



(45)

a nitrogen-oxygen bond cleavage to give an iminyl radical and an acyloxy radical and an oxygen-acyl bond cleavage to give an iminoxy radical and an acyl radical. Formation of iminyl and acyloxy radicals takes preference over oxygen-acyl bond cleavage. This is evidenced by the formation of carbon dioxide which results from the decarboxylation of the acyloxy radical.

While it can be seen that oxime carbamates are capable of photochemical transformation on irradiation, it should also be noted that their photochemistry could indeed be similar to that of composing functionalities. The photochemistry of other types of carbamates has been studied (75) in one way or the other. The irradiation of an alkyl N-arylcarbamate (46) gives an amine (47) and two photo-Fries rearrangement products (48) and (49).

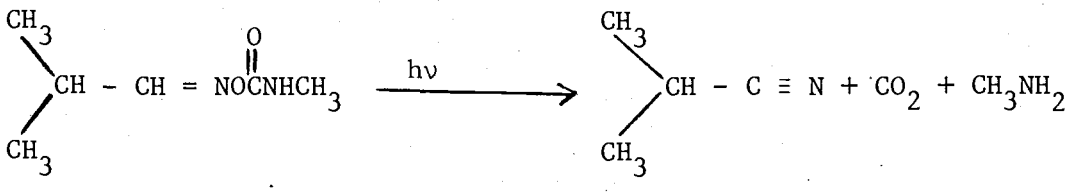


(46) (47) (48) (49)

While the photochemistry of other carbamate types has been studied, that of oxime carbamates, an important group of insecticidal carbamates, still remains relatively unknown.

RESULTS AND DISCUSSION

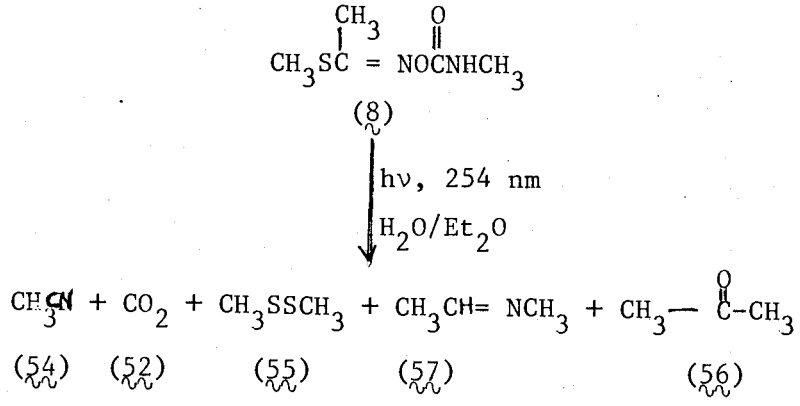
Earlier work on aldicarb (7) (76) and model systems provides guidelines under which the photochemistry of other oxime carbamates can be studied. The irradiation of isobutyraldehyde oxime (50) gave three products: isobutyronitrile (51), carbon dioxide (52) and methylamine (53). Based on established procedures for aldicarb and other model systems, it seemed possible that methomyl (8) would exhibit interesting photochemistry in either dilute organic or in dilute aqueous solutions.



(50) (51) (52) (53)

Irradiation of dilute aqueous solutions of methomyl (0.7 g, 0.004 mol in 100 ml of water) followed by a continuous liquid-liquid extraction with ether for 96h gave a mixture of six products as observed by gas chromatographic analysis. The products identified include: carbon dioxide (52), acetonitrile (54), (40%); dimethyldisulfide (55), (30%); acetone (56), (15%) and acetaldehyde methylimine (57), (5%). Other minor components present with less than 5% intensity were not identified. It is possible that methylamine (53) was not observed because of loss by evaporation or overheating. It is possible that many more products may have been formed but could not be identified because they were contained in the water layer.

This could be the case for water soluble components. The irradiation of more concentrated methomyl solutions (3% by weight) gave more products, but, significantly, those obtained in the photolysis of dilute aqueous solutions. It is possible that some of the products formed react further to give additional products. It was noted from the irradiation of aqueous solutions of aldicarb that immediate analysis of the reaction mixture was often difficult. It is for this reason that the later irradiation experiments of methomyl were carried out in organic solvents where such immediate analysis could be effected with minimum difficulty.



When methomyl (8) was irradiated (tetrahydrofuran, 254 nm) many more products were obtained as indicated by GC and GC-MS data collected (Figure 14). The GC-MS data obtained for some of the products is contained in Table IX at the end of this section. The products identified include carbon dioxide (52), methylamine (53) (40%), acetonitrile (54) (25%), dimethyldisulfide (55) (20%), and biacetylmethylhydrazone (58) (12%). Based on their GC-MS data, other

compounds present were tentatively identified as acetaldehyde methylhydrazone (58) (8%), and ethylenimine (57) (≤5%). No high molecular nitriles, oximes and dimerization products were observed in dilute tetrahydrofuran solutions of methomyl irradiated over short periods of times (1h - 4h). The same array of products was obtained when methomyl (8) was irradiated under similar conditions in acetonitrile. In acetonitrile, the major products obtained after six hours of irradiation are methylamine, dimethyldisulfide and biacetylmethylhydrazone. Minor traces of acetaldehyde methylhydrazone and ethylenimine were detected from their mass spectral data.

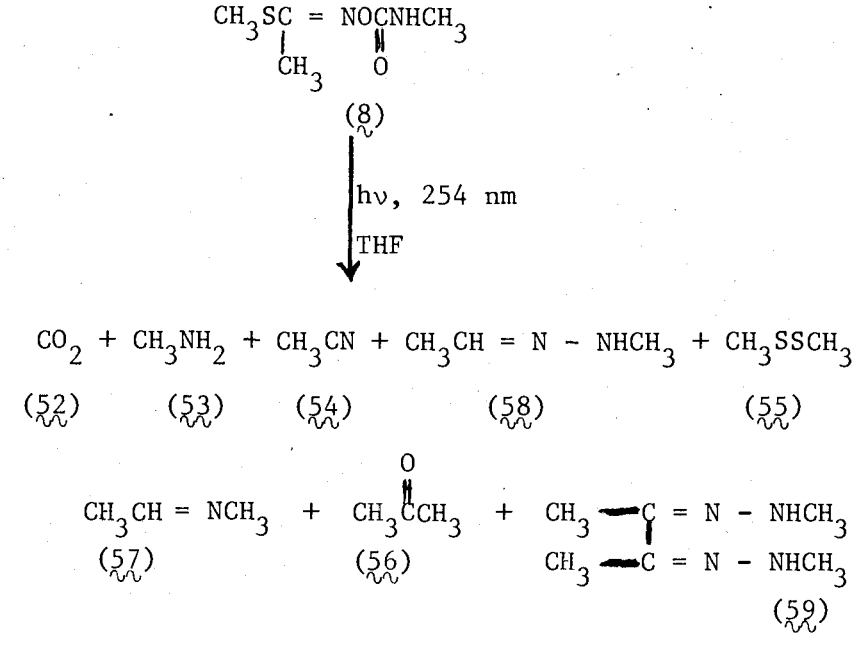


Figure 14. Photoproducts of methomyl from direct irradiation.

Similar experiments conducted in benzene, ethanol, isopropanol and methanol gave the same products to a greater or lesser extent. Also,

the photoreduction of benzene to cyclohexane seemed to be an important reaction when benzene solutions of methomyl were irradiated.

The irradiation of methomyl (8) in more concentrated solutions (6% by weight) with a Hanovia 450 watt mercury lamp gave an even greater number of products. In addition to some of the simpler products already observed, methomyl oxime (60), N,N'-dimethylurea (61), dimethylsulfoxide (62) methyl thioacetate (63) and methylthioacetimine (64) were tentatively identified using GC and GC-MS data. Even tentative assignments could not be given to two other components (m/e = 86 and 89). Whether some of the products obtained were the result of secondary photochemical reactions was not investigated. But, it was noted that the number of peaks observed varied with irradiation time. Peak intensities also varied with irradiation time. The photolysis of methylamine at 300 nm has been observed to give dimethylamine and ethylenimine (77).

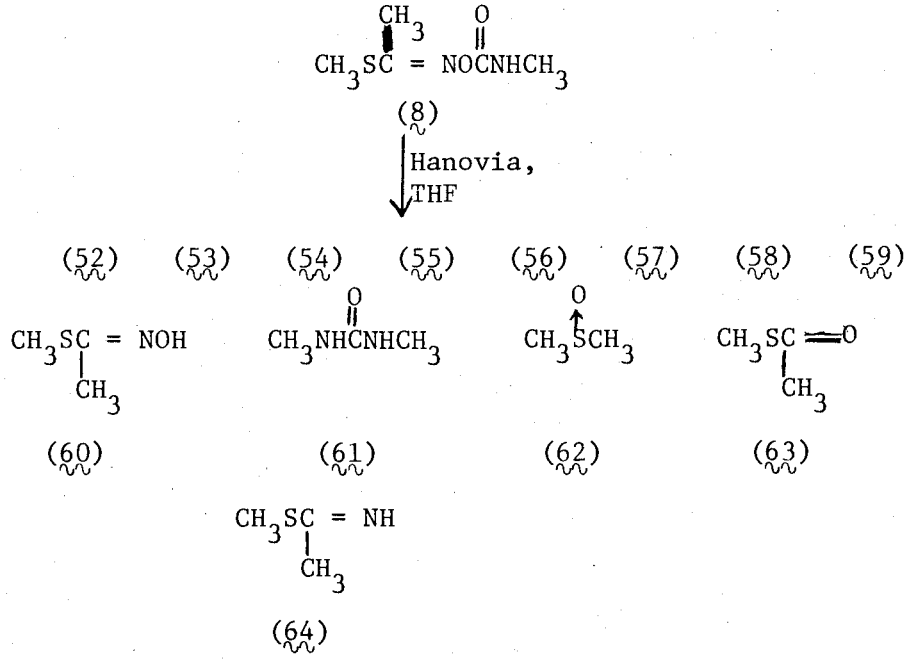


Figure 15: Direct Irradiation of Methomyl with Hanovia 450 watt lamp.

Not only was the irradiation of methomyl done directly, but it was also carried out in the presence of sensitizers. Three sensitizers, benzophenone, acetophenone and benzonitrile were used. When the irradiation was carried out using the three sensitizers in different solvents at 254 nm, the same array of products was obtained in each case to a greater or lesser extent (Eq. 20-22).

$$(8) \xrightarrow[\text{THF, PhCOPh}]{h\nu,\ 254\ nm} (52) + (53) + (54) + (55) + (59) \qquad \text{(Eq. 20)}$$

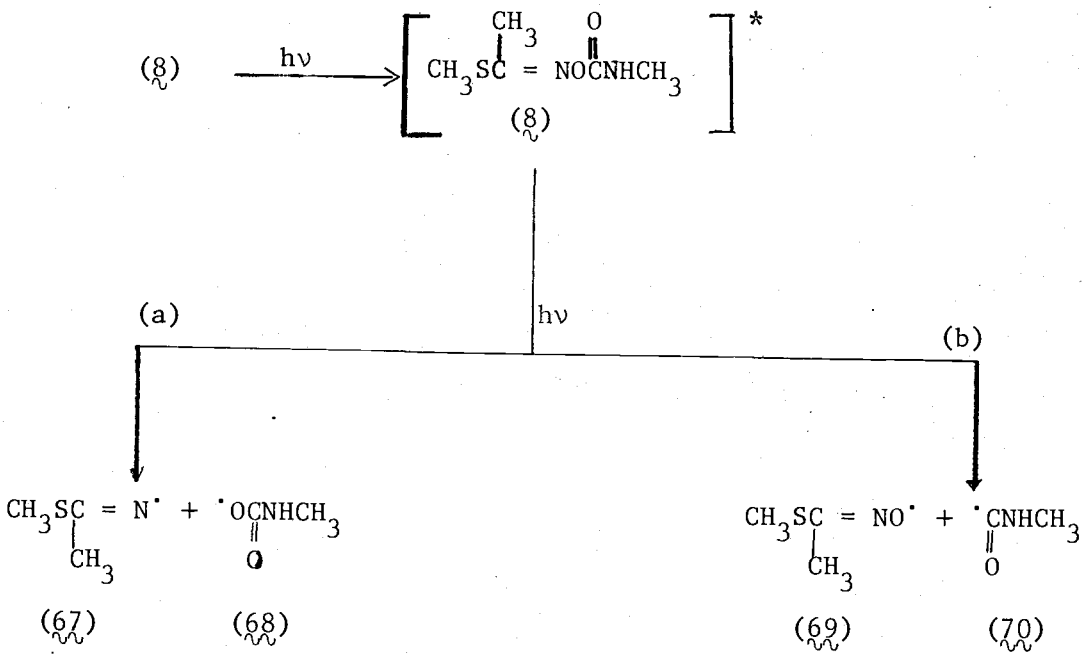
$$(8) \xrightarrow[\text{THF, PhCOMe}]{h\nu,\ 254\ nm} (52) + (53) + (54) + (55) \qquad \text{(Eq. 21)}$$

$$(8) \xrightarrow[\text{PhCN, EtOH}]{h\nu,\ 300\ nm} (53) + (54) + (55) + (59) \qquad \text{(Eq. 22)}$$

The yields observed were based on a comparison of peak heights to that of isoamyl alcohol (internal standard). These results suggest that the irradiation of methomyl whether direct or sensitized proceeds through a common product-forming intermediate. Further identification of products obtained was done by synthesizing the methylhydrazone of biacetyl (59). The photolysis of (59) at 254 nm gave a mixture of products: methylamine (53), acetonitrile (54) and the methylhydrazone of acetaldehyde (58).

The products obtained when methomyl (8) is irradiated can be explained in part by two bond cleavages: (a) a nitrogen-oxygen bond cleavage generating an iminyl and an acyloxy radical, and (b) an oxygen-acyl bond cleavage generating an iminoxy radical and an acyl radical. Subsequent cleavages such as the carbon-sulphur bond, the

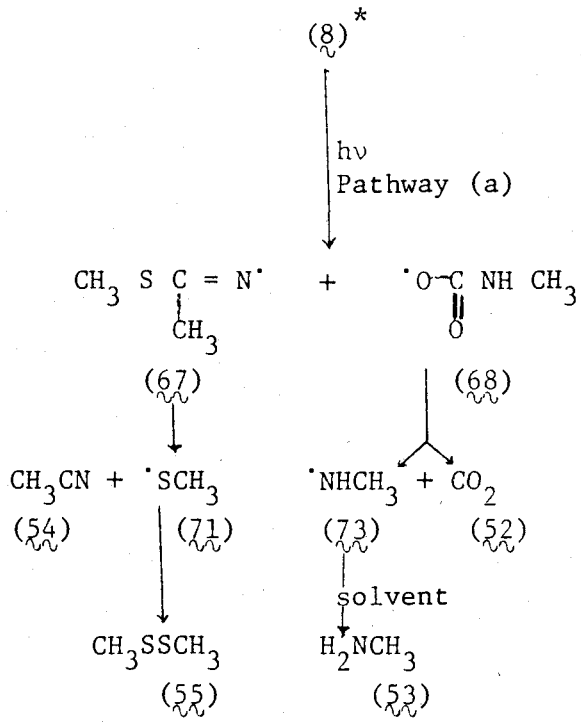
carbon-nitrogen bond, are possible but are not necessarily primary processes in product generation. The carbon-sulphur bond cleavage occurs with relative ease (76). Pathways (a) and (b) (Scheme I) are the major routes with (a) taking preference over (b) as evidenced by the formation of carbon dioxide (the result of decarboxylation of the acyloxy radical).



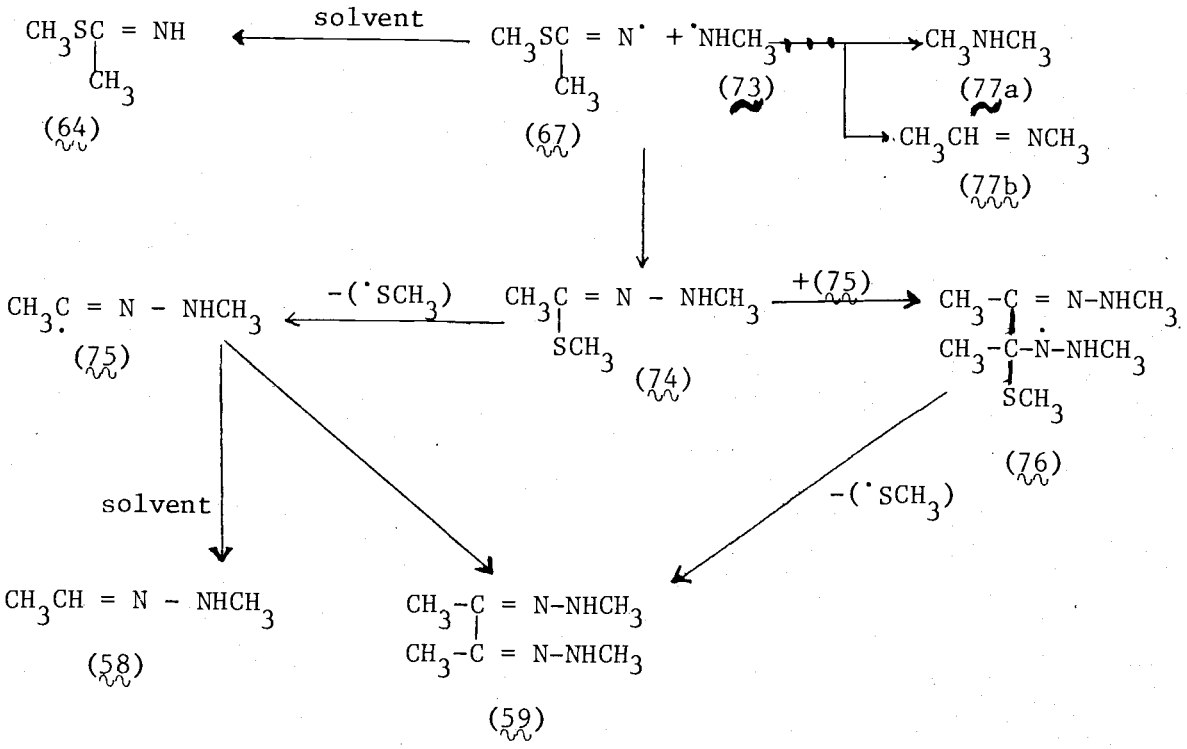
Scheme I

Subsequent to fission as illustrated in Scheme I radicals (67) and (68) undergo further reactions (pathway a) (Scheme IIa). The methylthio iminyl radical (67) loses the methylthio radical to give acetonitrile (54). The methylthio radical (71) gives dimethyldisulfide (55)

through dimerization or radical recombination. The acyloxy radical (68) gives radical (73) and carbon dioxide (52). The methylamino radical (73) picks up a hydrogen atom to give methylamine (53). Radical (73) can also combine with radical (67) to give (74) (Scheme IIb). The methylhydrazone of methylthioacetate (74) loses the methylthio radical (71) to give radical (75). The iminyl radical (75) can either add to compound (74) to form the intermediate (76) which loses a methylthio radical to give (59), or it picks up a hydrogen atom from the solvent to give acetaldehyde methylhydrazone (58). The methylamine formed is capable of further reactions giving



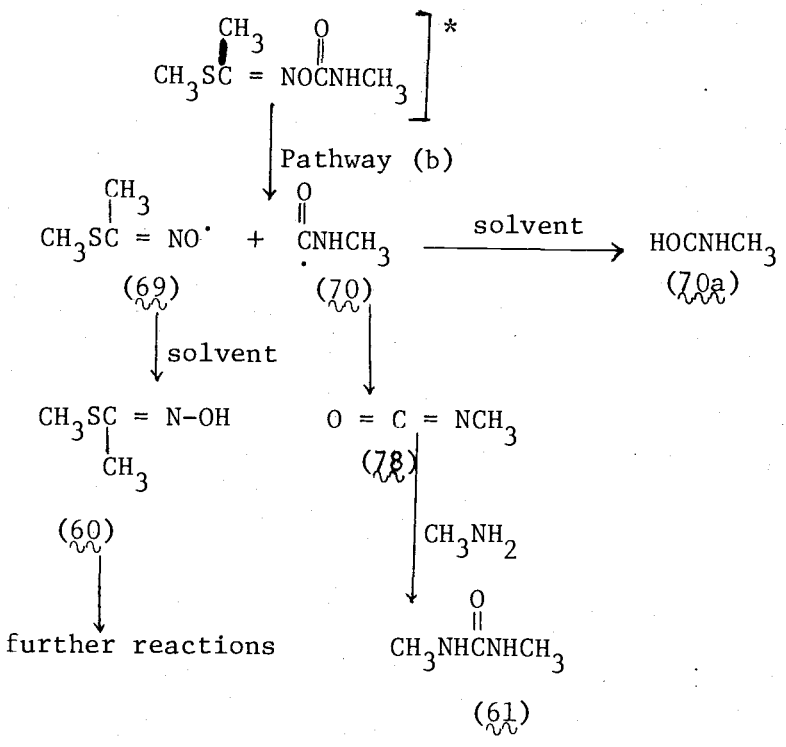
Scheme IIa



Scheme IIb

dimethyl amine (77a) and ethylimine (77b). Radical (67) picks up a hydrogen atom from solvent forming the thioketimine (64) which can be hydrolyzed to give the thioester (63).

Other products formed in the irradiation of methomyl (8) can be explained using the cleavage pattern of pathway (b) (Scheme III). The iminoxy radical (69) formed picks up a hydrogen atom from solvent to give the methomyl oxime (60). The oxime (60) is capable of further photochemical or thermal decomposition reactions. The oxime (60) was not isolated but preliminary investigations of its photolysis in tetrahydrofuran (λ = 254 nm) gave methylthiocyanide, acetonitrile, methylthioacetate, dimethyldisulfide and two unidentified peaks (m/e,



Scheme III

88 and 103). The radical (70) gives methylisocyanate (78) by hydrogen loss (perhaps to (70a) within a solvent cage. The methylisocyanate (78) formed in the presence of methylamine gives N,N-dimethylurea (61).

Quantum yields were determined to provide additional characterization of the photochemical processes under observation and are summarized in Tables I, II, III, IV, V and VI. The percent yields calculated are based on the relation:

$$\text{Percent Yield} = 100\left(\frac{\Phi_x}{\Phi_x + \Sigma\Phi_i}\right)$$

Φ_x: quantum yield of product of interest.

$\Sigma\Phi_i$ represents the summation of the quantum yields of all other competing reactions. This corresponds to the amount of product X relative to all products and is not the percent of the starting material converted to product X. This is given by $\Phi_x I_a / C_o$, where C_o is number of moles of reactant; I_a = intensity of radiation absorbed) (77b).

Table I. Quantum Yields of Photoproducts in Tetrahydrofuran (λ=254 nm)

Product	Quantum Yield[(a)]	Standard Deviation	Percent Yield
*CO_2	--	--	--
CH_3NH_2	0.93	0.09	38%
CH_3CN	0.68	0.09	28%
CH_3SSCH_3	0.73	0.07	30%[(b)]
$CH_3-C=N-NHCH_3$ $CH_3-C=N-NHCH_3$	0.13	0.00	5%[(b)]

[a]Quantum yields determined using cyclopentanone actinometry and at λ = 254 nm.

[b]Percent Yield based on 0.5 mole per mole of methomyl.
*Amount produced or quantum yield was not determined.

Table II. Quantum Yields of Photoproducts in Tetrahydrofuran and Sensitized with Benzophenone with λ = 254 nm.

Product	Quantum Yields	Standard Deviation	Percent Yield
CO_2	--	--	--
CH_3NH_2	0.91	0.11	32%
CH_3CN	0.88	0.02	31%
CH_3SSCH_3	0.87	0.01	30%
$CH_3-C(=N-NHCH_3)-CH_3$ $CH_3-C=N-NHCH_3$	0.200	0.01	7%

Table III. Quantum Yields of Photoproducts in Tetrahydrofuran with Hanovia lamp

Product	Quantum Yield	Standard Deviation	Percent Yield
CO_2	--	--	--
CH_3NH_2	0.09	--	3.3%
$(CH_3)_2NH$	0.11	--	4.1%
CH_3CN	0.97	--	35 %
$CH_3CH=NNHCH_3$	0.43	--	16 %
CH_3SSCH_3	0.80	--	29 %
$CH_3-C(=NNHCH_3)-CH_3$ $CH_3-C=NNHCH_3$	0.34	--	12 %

Table IV. Quantum Yields of Photoproducts in Acetonitrile, λ = 254 nm.

Product	Quantum Yields	Standard Deviation	Percent Yield
CO_2	--	--	--
CH_3NH_2	0.04	0.001	4.2%
CH_3CN	***	***	***
CH_3SSCH_3	0.71	0.02	82 %
$CH_3SC(CH_3)NNHCH_3$	0.05	0.02	6 %
$CH_3-C(=N-NHCH_3)-CH_3$	0.07	0.02	8 %

Table V. Quantum Yields of Photoproducts in Acetonitrile Sensitized with Benzophenone with λ = 254 nm.

Product	Quantum Yield	Standard Deviation	Percent Yield
CO_2	--	--	--
CH_3NH_2	0.017	0.002	1.77
CH_3CN	***	***	***
CH_3SSCH_3	0.659	***	68.50
$CH_3SC(CH_3)NNHCH_3$	**	**	**
$CH_3-C(=NNHCH_3)-CH_3$	0.286	0.0143	29.70

***Solvent; **Could not be determined

Table VI. Quantum Yields of Photoproducts in Methanol with λ = 254 nm Sensitized with Benzophenone.

Product	Quantum Yield	Standard Deviation	Percent Yield
CO_2	--	--	--
CH_3NH_2	0.115	0.0287	11.80
CH_3CN	0.837*	0.279*	85.60
CH_3SSCH_3	***	***	***
$CH_3-C(=N-NHCH_3)-CH_3$	0.026	0.0064	2.70

***Could not be determined; *unreliable

It can be noted from the tables of quantum yields of photo products of methomyl in various solvents that those in tetrahydrofuran are significantly higher than quantum yields in acetonitrile and methanol. The sum of product quantum yields in acetonitrile and methanol. The sum of product quantum yields indicated in Table III seems to suggest that a chain mechanism could be involved. Another possibility could be that some of the products formed react further to give more products (compare quantum yields for methylamine and dimethylamine). Also quantum yields in excess of unity are not uncommon (77b). Whether or not there is a relationship between solvent polarity and the mechanism for product formation was not determined although α,β-unsaturated esters show the "photodesmotic" effect (78). One general observation is the fact that reactions in benzene and tetrahydrofuran tended to proceed better than in acetonitrile or methanol. Photoreduction of benzene to cyclohexane

was observed as an important reaction through MS analysis. The "photodesmotic" effect implies bond formation through the absorption of light. The wavelengths of maximum absorption of methomyl are 233 nm in methanol, 236 nm in acetonitrile, and 232 nm in tetrahydrofuran as determined by ultraviolet spectroscopy. No such dependence on solvent type and on solvent properties (solvent polarity) was observed in this study.

Quantum yields, as can be seen, are slightly higher or unchanged when sensitizers are used. It is probable that the triplet excited state is the product determining excited state. This was investigated further by studying the quenching effects on the quantum yields of photoproducts. The results are summarized in Tables VII and VIII. Using isoprene as the triplet state quencher, the data of Tables VII and VIII were obtained. The resulting Stern-Volmer plot of the ratio of quantum yields in the absence and presence of a quencher against varying quencher concentrations was obtained. The plot of the data of Table VII is observed to be linear, a fact which supports the involvement of the triplet excited state in product formation. The interpretation of these results is based on a Stern-Volmer formulation for quenching of unimolecular reactions of an excited state to give the approximate expression (79):

$$\frac{\Phi_o}{\Phi} = 1 + k\,[Q]$$

Φ_o = quantum yield in absence of quencher,

Φ = quantum yield in presence of quencher.

A correlation coefficient of 0.975 (0.98) is obtained when the ratio of quantum yields in the absence and presence of the quencher are plotted against varying quencher concentrations. At higher quencher concentrations, a significant positive deviation is observed. These results are comparable to those obtained in simple ketone systems. Energy transfer from the triplet excited state is known to be diffusion-controlled. At low quencher concentrations, the quencher molecules are far from the substrate and so they must diffuse some distance. At higher quencher concentrations, the quencher molecules are very close to the substrate molecules and in some cases, little or no diffusion is required for quenching. Therefore, the quenching rate is faster at higher quencher concentrations than at lower concentrations. Hence, the initial slope at lower concentrations could be attributed to normal triplet quenching. The deviation at higher quencher concentrations could be the result of static quenching which is known to occur (80, 81).

Table VII. Quenching Effects on Quantum Yields (λ = 300, THF).

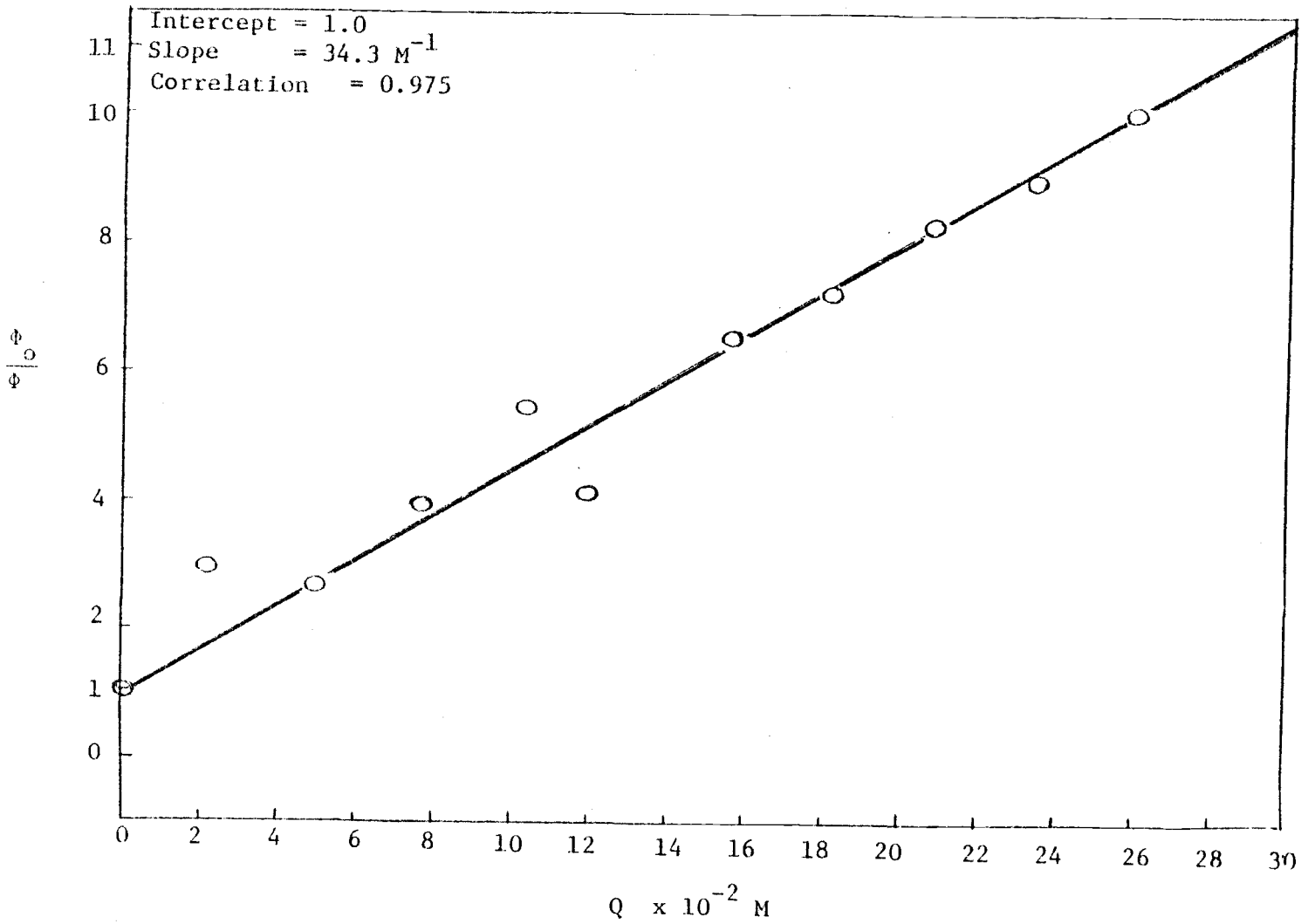
$Q \times 10^{-2}M$	Φ	Φ^{-1}	Φ_o/Φ	(Value plotted)*
0.000M	1.802[a]	--	1.00	
2.060	0.6096[b]	1.640	2.9560	(2.96)
5.200	0.6315	1.590	2.8535	(2.85)
7.800	0.4611	2.170	3.9081	(3.91)
10.400	0.3340	3.030	5.3952	(5.40)
12.000	0.4465	2.220	4.0358	(4.04)
15.600	0.2836	3.570	6.3540	(6.35)
18.200	0.2500	4.000	7.2080	(7.21)
20.800	0.2173	4.550	8.2927	(8.19)
23.400	0.2073	4.760	8.6927	(8.69)
26.000	0.1790	5.560	10.0670	(10.07)

[a]This is the value for Φ_o based on at least 90% conversion after 31h.

[b]Φ in the presence of quencher, determination based on disappearance of starting material.

Stern-Volmer plot: I: Φ_o/Φ versus Quencher concentrations.

*The values in brackets are the actual values plotted. Although no standard deviations are given, each value is the average of three runs.



Stern-Volmer Plot (I): Quenching Effects in Photoproduct Quantum Yields at Low Quencher Concentrations.

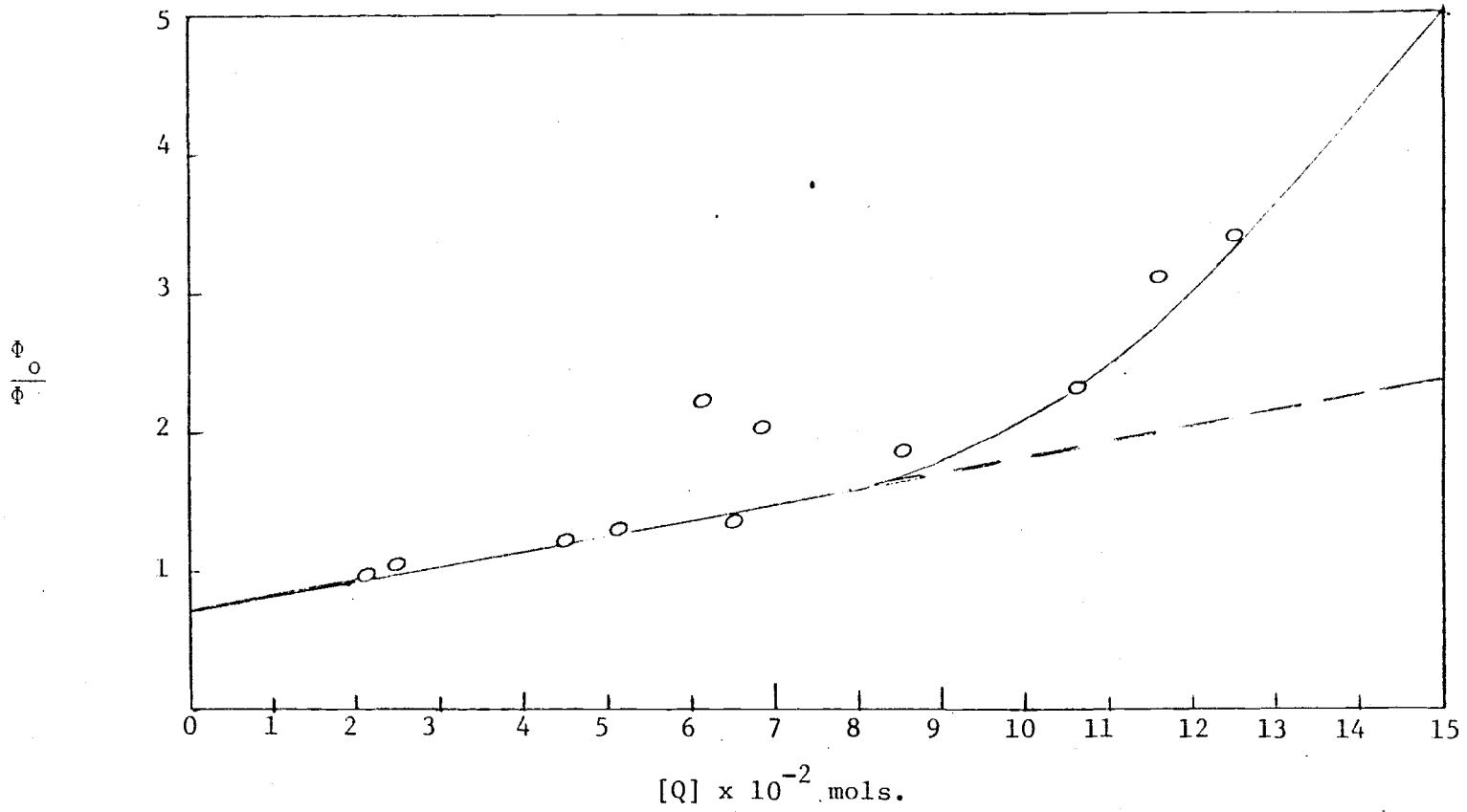
Table VIII. Quenching Effects on Photoproduct Quantum Yields at Higher Quencher Concentrations. (λ = 300 nm; solvent: tetrahydrofuran).

Q x10^{-2} moles	Φ	Φ^{-1}	Φ_o/Φ
0.0000 moles	0.940[a]	--	1.000
2.0954	0.995[b]	1.005	0.945
2.3437	0.935	1.070	1.001
4.4062	0.783	1.277	1.201
5.0602	0.711	1.407	1.322
6.0533	0.438	2.283	3.146
6.5326	0.730	1.370	1.288
6.8600	0.465	2.151	2.022
8.4784	0.518	1.931	1.815
10.5916	0.409	2.445	2.298
11.6310	0.308	3.247	3.052
12.5514	0.279	3.584	2.369

[a] Φ_o: Quantum yield in the absence of isoprene.

[b] Φ: Quantum yields in the presence of varying quencher concentrations. Each value is the average of three runs.

NOTE: The failure of quantum yields determined by disappearance of starting material and those determined by product formation to correspond could be the result of one or several reasons, for example coupling of radicals and dimerization. The disappearance of starting materials is independent of these reactions. Ref: Herweh, J.E., and C. E. Hoyle, J. Org. Chem., 45, 2195, 1980.



Stern-Volmer Plot (II): Quenching Effects on Quantum Yields of Photoproducts at Higher Quencher Concentrations.

Similar studies on aldicarb (7) gave much the same results. Aldicarb (7), when photolyzed in acetonitrile with Rayonet 254 nm lamps gave a mixture which included: methylamine, dimethyldisulfide, tetramethylsuccinonitrile, N,N'-dimethylurea, 1-methylthio-2,3-dicyano-2,3-dimethylbutane, dimethylamine, methylthioisobutyronitrile and the oxime of aldicarb. Reactions sensitized with benzonitrile with light greater than 254 nm gave four products: methylamine, dimethyldisulfide, 1-methylthio-2,3-dicyano-2,3-dimethylbutane and tetramethylsuccinonitrile (76). The conclusion is that the photochemical transformation of aldicarb (7) proceeds to products principally through the triplet excited state. The nitrile (79) and the oxime (82) were shown in later studies to be the result of thermal decomposition in the column during analysis.

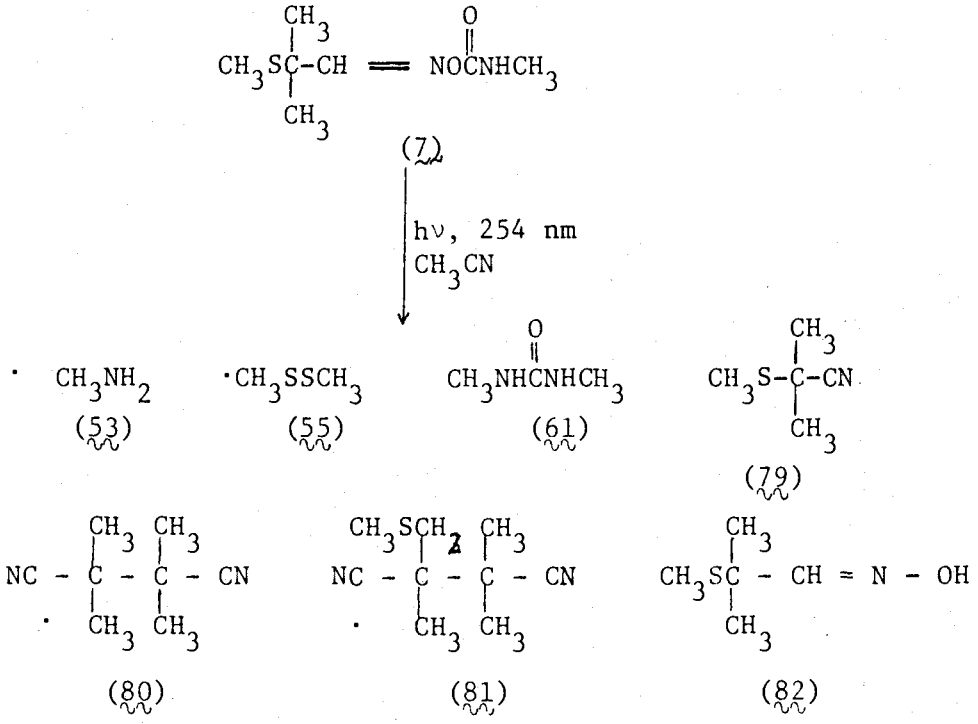
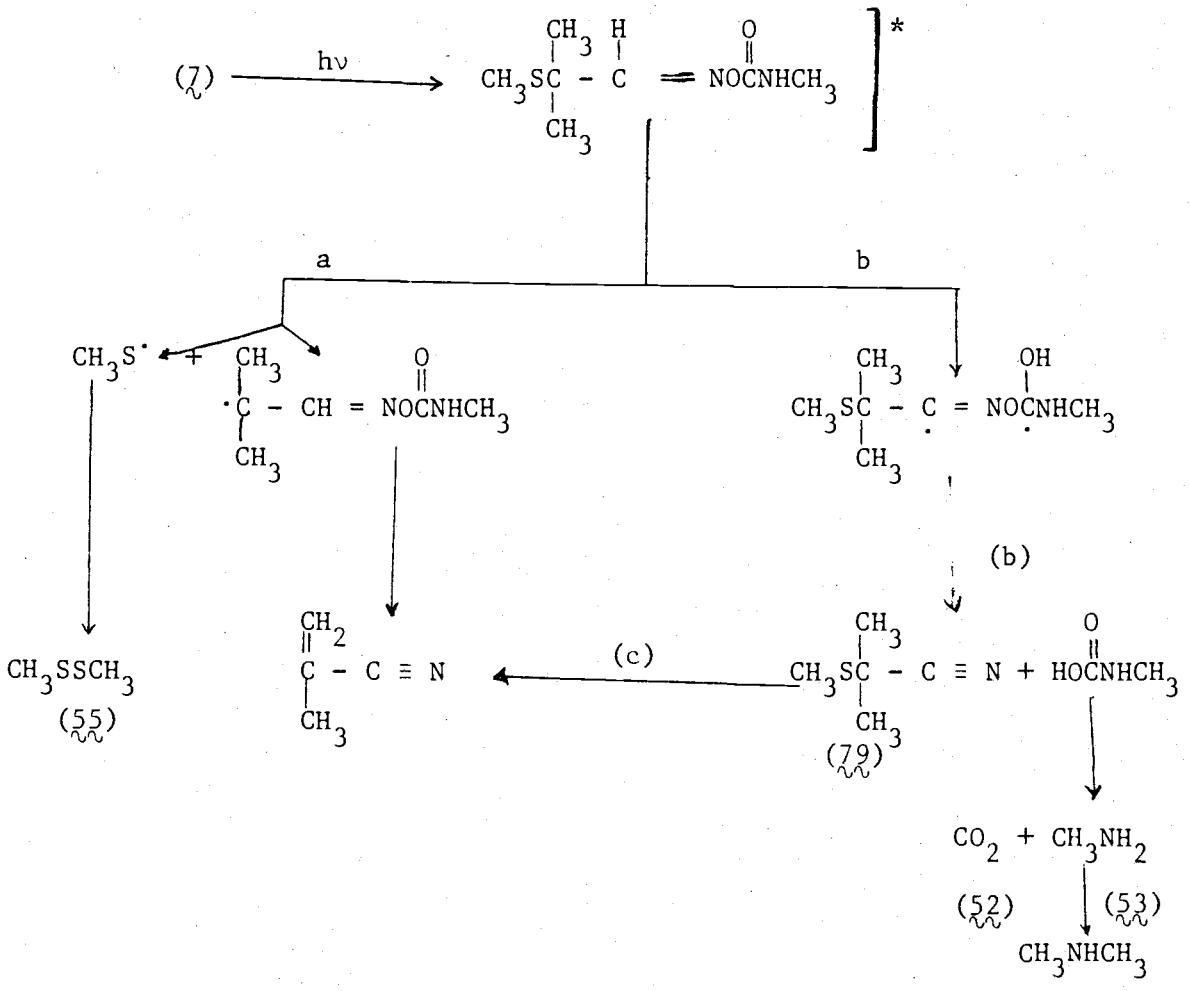
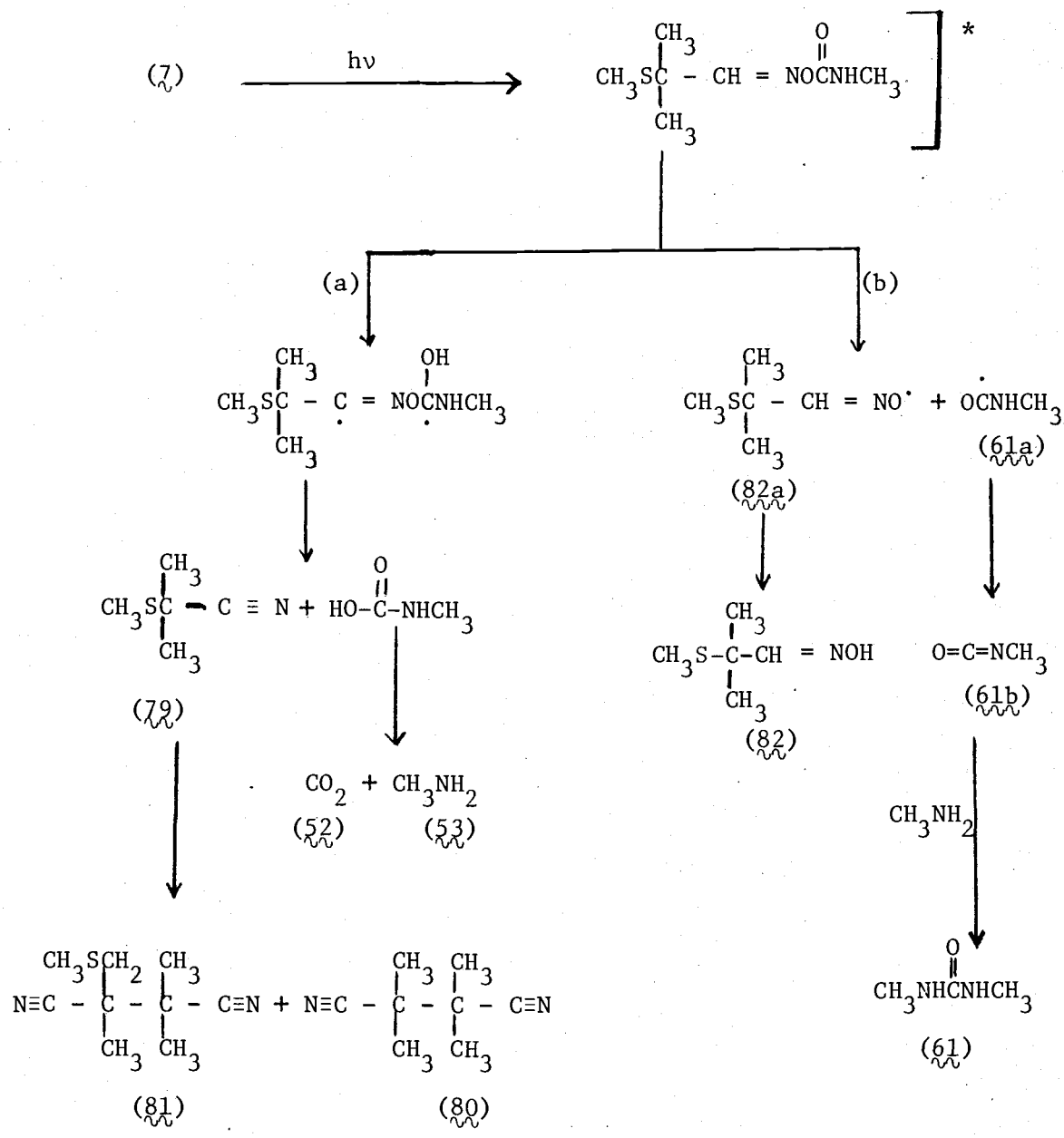


Figure 16 Photoproducts of Aldicarb.

The products obtained in aldicarb (7) photolyses suggest that both nitrogen-oxygen and acyl-oxygen cleavages are major reaction pathways. An intramolecular hydrogen abstraction in the excited substrate which results in the formation of a diradical, which then undergoes nitrogen-oxygen fragmentation (route b, Scheme IV) has been suggested (76). Dimethyl disulfide is formed by both routes (a) and (b).

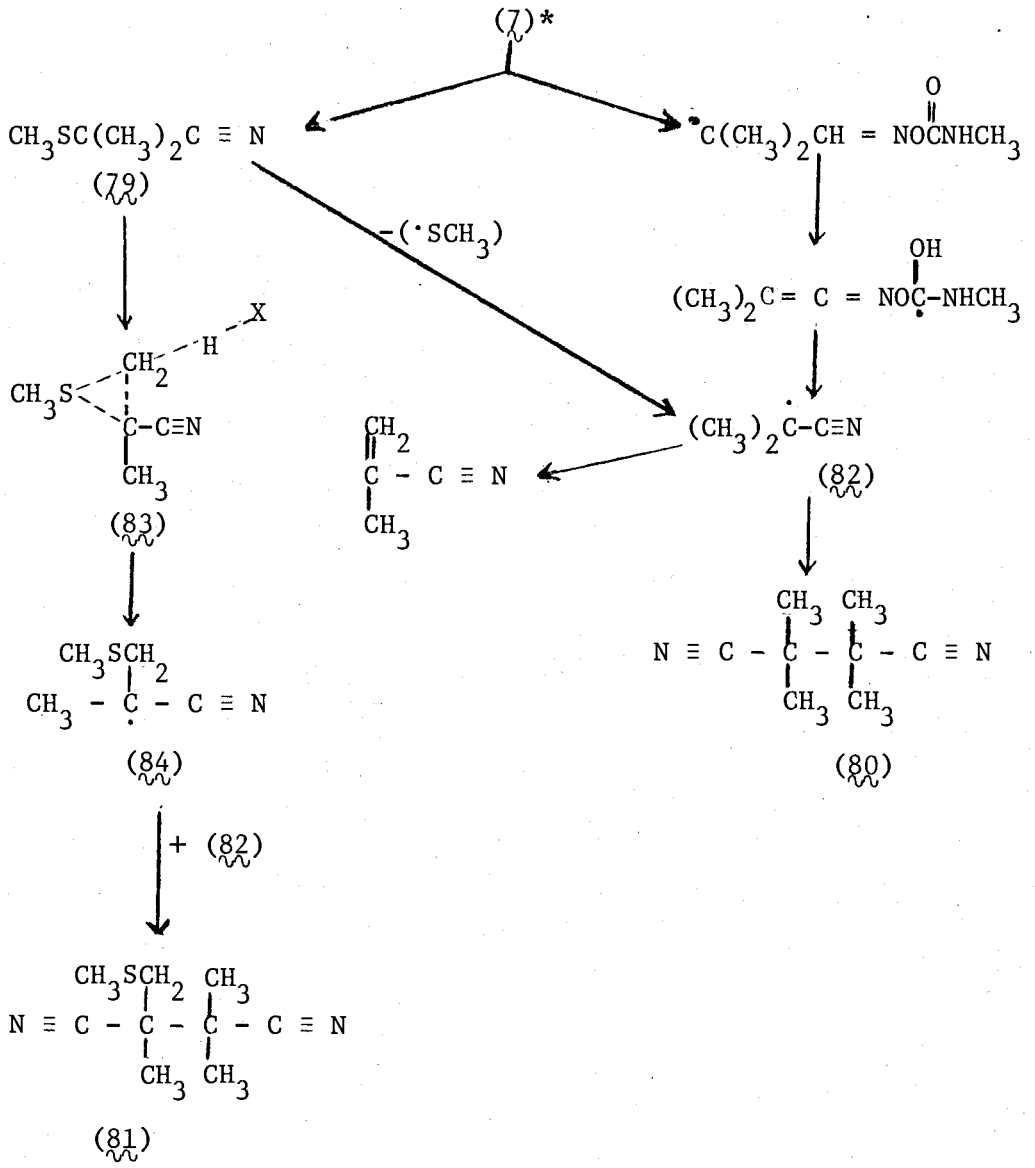


Scheme IV



Scheme V

Thus, the formation of methylamine as well as the dinitriles (81) and (80) may be explained as a result of nitrogen-oxygen fission (pathway (a) in Scheme V). Acyl-oxygen cleavage (pathway (b), Scheme V) on the other hand, generates radicals (82a) and (61a) which


(7)*
CH3SC(CH3)2C ≡ N
(79)
-(·SCH3)
·C(CH3)2CH = NOCNHCH3
O
(CH3)2C = C = NOC-NHCH3
OH
(CH3)2C-C≡N
(82)
CH2
C - C ≡ N
CH3
X
H
CH2
CH3S
C-C≡N
CH3
(83)
CH3SCH2
CH3 - C - C ≡ N
(84)
+ (82)
CH3SCH2 CH3
N ≡ C - C - C - C ≡ N
CH3 CH3
(81)
CH3 CH3
N ≡ C - C - C - C ≡ N
CH3 CH3
(80)

Scheme VI

can transfer a hydrogen within a solvent cage to produce the oxime (82) and methylisocyanate (61b), the latter reacting with methylamine to form N,N'-dimethylurea (61). Oxime (82) may contribute to the formation of nitrile (79). Returning to consider the details of route (a), Scheme VI, nitrile (79) has two reasonable options: it might lose a methythio radical to give radical (82), which then dimerizes forming tetramethylsuccinonitrile (80), or it can undergo a hydrogen abstraction through a bridged sulfide transition state (83) to form radical (84). Radical (84) once formed can couple with radical (82) to give 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane (81) (Scheme VI). Recombination of radicals of this nature has been observed in the decomposition of azobisisobutyronitrile (82).

It can be seen from the foregoing discussion that the bond cleavages as a result of photolysis are common to both aldicarb (7) and methomyl (8). Based on results of irradiation experiments for aldicarb (7) and methomyl (8), the following conclusions can be made: (a) the product spectrum obtained is often diverse; (b) the photochemical transformation of aldicarb (7) and methomyl (8) proceeds largely through the triplet excited state; (c) the major decomposition pathway involves nitrogen-oxygen bond cleavage with acyl-oxygen bond fission as the minor pathway; (d) the efficiency of product formation depends on the product being determined; (e) oxime carbamates indeed undergo both sensitized and unsensitized photoinduced reactions.

TABLE IX. GC-MS Data for Photoproducts of Methomyl.

Compound Name and Structure	m/e	% Relative Intensity
Methylamine, CH_3NH_2	15	21
	18	a
	26	b
	27	16
	28	80
	29	58
	30	19
	31	100
	32	54
	33	5
Acetonitrile, CH_3CN	38	10
	39	25
	40	54
	41	100
	42	25
Carbon Dioxide, CO_2	16	7
	22	a
	28	24
	30	a
	31	a
	44	100
	45	1
	46	1
S-methylthioacetate, $CH_3-\underset{\underset{SCH_3}{\vert}}{C}=O$	28	10
	43	100
	45	17
	47	13
	90	25
	91	11
Dimethyldisulphide, CH_3SSCH_3	32	27
	45	55
	56	41
	57	39
	61	14
	64	24
	79	53
	94	100
	96	8
Biacetyl methylhydrazone, $CH_3-\underset{\underset{CH_3-C=N-NHCH_3}{\vert}}{C}=N-NHCH_3$	15	29
	27	18
	35	13
	45	100[b]
	46	57
	47	93

Table IX. GC-MS Data for Photoproducts of Methomyl (Continued).

Compound Name and Structure	m/e	% Relative Intensity
Biacetyl methylhydrazone	48	13
	61	38
	62	67
	64	15
	79	57
	94	84[b]
	96	14
	127	36
	141	11
	142	79[b]
	143	(2)

[a]These values could have been listed except for the fact that only values with ten or greater than ten percent intensity have been included. They were observed and are present in the spectrum.

[b]These values varied in intensity but were observed every time the mass spectrum was obtained

Table X. UV Data of Methomyl and Biacetylmethylhydrazone

Compound	Solvent	$\lambda_{max(nm)}$	$\varepsilon(\ell\ mol^{-1}\ cm^{-1})$
Methomyl	Acetonitrile	236	5339[a]
	Methanol	233	10076
	Tetrahydrofuran	232	4225[a]
Biacetyl-methyl-hydrazone	Methanol	286.5	14274

[a]These values have been corrected for solvent absorption.

Table XI. ^{1}H-NMR Data of Some Compounds.

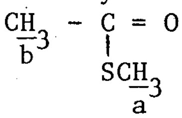
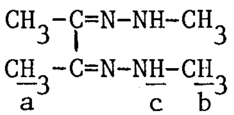
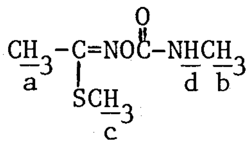
Compound	Solvent	Chemical Shifts
S-methylthioacetate 	$CDCl_3$	a: 2.28 (Singlet, 3H) b: 2.32 (Singlet, 3H)
Biacetylmethyl-hydrazone 	$CDCl_3$	a: 1.89 (Singlet, 6H) b: 2.96 (Singlet, 6H) c: 4.5-5 (2H)
Methomyl 	$CDCl_3$	a: 2.20 (Singlet, 3H) b: 2.85 (Singlet, 3H) c: 2.44 (Doublet, 3H) d: 6.2 (Singlet, 1H)

Table XII. ^{13}C-NMR Data for Some Compounds

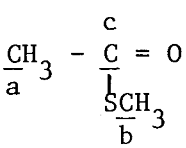
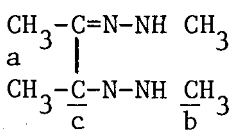
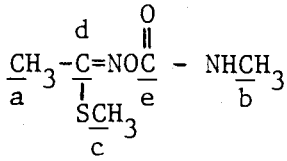
Compound	Solvent	Chemical Shifts
S-methylthioacetate 	$CDCl_3$	a: 11.76 ppm b: 30.27 ppm c: 195.72 ppm
Biacetylmethyl-hydrazone 	$CDCl_3$	a: 9.00 ppm b: 38.27 ppm c: 144.82 ppm

Table XII. ^{13}C-NMR Data for Some Compounds (Continued)

Compound	Solvent	Chemical Shifts
Methomyl 	$CDCl_3$	a: 13.46 ppm b: 18.99 ppm c: 27.63 ppm d: 155.62 ppm e: 160.66 ppm

EXPERIMENTAL

Instrumental Methods

Chromatographic Analyses

In initial analytical work, a programmable Varian Aerograph Series 1200 gas chromatograph equipped with a flame ionization detector was employed. Nitrogen was used as the carrier gas. In subsequent analyses a programmable Varian Chromatograph Model 3700 Series equipped with both flame ionization and thermal conductivity detectors was used. Helium was used as the eluent gas. The following columns were used during analysis: (A) 10' x 1/4" OD 5% Carbowax 20M aluminum column on chromosorb G NAW 60/80 mesh; (B) 20' x 1/8 " OD 5% Carbowax 20 M aluminum column on chromosorb W AW 60/80 mesh; (C) 15' x 1/8" OD 10% Carbowax 20 M - 2% KOH copper column on Anakrom ABS 70/80 mesh; (D) 5' x 1/8" OD 10% Carbowax 1500 aluminum column on chromosorb W 60/80 mesh; (E) 19' x 1/8" OD 20% Carbowax 20 M aluminum column on Anakrom ABS 70/80 mesh; (F) 2m x 1/8" OD 10% Dinonyl phthalate aluminum column on chromosorb W AW DMCS 80/100 mesh for Varian Series 1200 chromatograph (GC-MS analyses); (H) 10' x 1/8" OD 10% Dinonyl phthalate aluminum column on chromosorb W AW DMCS 80/100 mesh for Varian model 3700 Series chromatograph.

High Pressure Liquid Chromatography (HPLC) analyses were effected using a Liquid Chromatograph from Water Associates fitted with a Model 660 Solvent Programmer and an ultraviolet Model 440 Absorbance Detector. In direct phase HPLC analysis, the following conditions

were used: column material, spherisorb (SS); column length-25 cm OD, 4.6mm ID; column packing-Lichrosorb silica; particle size and frit-5μ and 0.5μ respectively; flow rate - 1 ml/min; solvent system -dichloromethylene (DCM), methanol, Isoctane (TMP). For reversed phase HPLC analysis a 50:50 acetonitrile water mixture was used as the eluent system.

Mass Spectrometry

Columns (A) (E) and (G) were used for GC-MS analyses. Direct mass spectral and GC-MS data were obtained using a CH7 mass spectrometer fitted with a Varian Aerograph Series 1200.

Infrared and Ultraviolet Spectroscopy

Infrared spectra were obtained on a Perkin-Elmer 727B Infrared Spectrophotometer. Ultraviolet-visible spectra were obtained on a Cary 118 spectrophotometer and also on a Beckman DB Spectrophotometer.

Nuclear Magnetic Resonance Spectroscopy (NMR)

The proton NMR spectra were obtained using a Varian HA-100 unit, while Carbon-13 NMR spectra were obtained on a Varian CFT-80A instrument.

Elemental Analyses

Elemental Analyses were performed by Dr. Johnson of MICANAL Inc., of Tempe, Arizona.

Photolyses and Quantum Yields

Sample irradiation was carried out in a Rayonet Type RS Preparative Photochemical Reactor from the Southern New England Ultraviolet Company Rayonet using 2537 A^{o} and 3000 A^{o} mercury lamps or in a reactor using a Hanovia 450 watt high pressure mercury lamp without filters. Samples were contained in 13 mm-Pyrex or Quartz resealable tubes or in appropriate photochemical quartz containers.

Quantum yields were run in a merry-go-round apparatus using a suitable choice of radiant energy source. Product quantities for calculation of quantum yields were determined from gas chromatographic data based on relative peak areas compared to that of an internal standard (isoamyl alcohol) measured with a Hewlett-Packard 3373 B Digital Integrator connected to a Model GC 3700 Varian Chromatograph.

Solvent Purification

The need for reproducibility of results and elimination of possible side reactions favoured by solvent impurities cannot be overemphasized. Acetonitrile, benzene and tetrahydrofuran (THF) were purified according to the procedures described below. Photrex methanol for UV spectrophotometry and absolute ethanol, USP quality, were used without purification. Isopropanol (technical grade) was used without purification.

Purification of Acetonitrile

About 1000 ml of reagent grade acetonitrile were stirred with calcium hydride until gas evolution ceased. The mixture was filtered and the filtrate was distilled from P_2O_5 (about 5g/ℓ) in an all glass apparatus using a high reflux ratio. The distillate was then refluxed over calcium hydride (CaH_2, 5g/ℓ) for at least an hour after which it was distilled slowly discarding the first 5% and last 10% of the distillate so as to reduce acrylonitrile content. No azeotropic distillation was done as benzene was not an impurity.

Purification of Benzene

A more routine purification was achieved by shaking and stirring a liter of benzene with concentrated sulfuric acid (approximately 100 ml/ℓ of benzene). The acid layer was then removed and the procedure repeated until there was no darkening of the sulfuric acid layer. The benzene was then decanted, washed with distilled water and then dried with $MgSO_4$. The magnesium sulphate ($MgSO_4$) was then filtered off and the filtrate distilled in an all glass apparatus.

Purification of Tetrahydrofuran

Metallic sodium and a suitable amount of benzophenone were added to about 700 ml of reagent grade THF. This was then heated slowly in a nitrogen atmosphere until the mixture turned blue. The mixture was then refluxed for an additional hour and the distillate collected thereafter.

Direct Irradiation of Methomyl (8)

Photolysis of Methomyl (8) in Water with λ=254 nm.

A solution of methomyl (0.7 g, 0.004 mol) was prepared in 100 ml of water. Portions of 6 ml each were introduced into 8 resealable quartz tubes, then degassed by 4 freeze-thaw cycles. The samples were then irradiated for 10h using Rayonet 254 nm lamps. At the end of irradiation, the samples were refrigerated, then the contents were transferred into a 100 ml round bottom flask and extracted continuously with ether for 96h. The extract was then concentrated to 25 ml and the final solution chromatographed using column B at 70° providing evidence for seven components. The seven components were analyzed by GC-MS using column B at 70°: A, m/e = 44, carbon dioxide, B, m/e = 57 methylimine of acetaldehyde; C, m/e = 58, acetone; D, m/e = 60, not identified; E, m/e = 74 ether; F, m/e = 41, acetonitrile; G, m/e = 94, dimethyldisulfide. Peaks obtained with less than 5% intensity were not identified. Identification of carbon dioxide (m/e, 44) was based on comparison of its glc retention time (columns F, 60/80 mesh, 60°) with that of an authentic sample. The amount of carbon dioxide was not determined. Acetonitrile, acetone, and dimethyldisulfide were identified by comparison of their mass spectral data with those of published spectra (84).

Photolysis of Methomyl (8) in Acetonitrile with λ-254 nm.

A 100 ml solution of methomyl (3.24 g, 0.02 mol) in acetonitrile was prepared. About 6 ml portions of the sample solution

were placed in four resealable quartz tubes and degassed by a series of freeze-thaw cycles. The samples were irradiated with Rayonet 254 nm lamps for 6h. Gas chromatographic and GC-MS analyses on column B at 60-250°C gave 6 peaks. Some of the peaks were identified to be the same as those obtained in the irradiation of methomyl in water. Peak 2 (m/e = 31) by comparison of its mass-spectrum with that of an authentic sample and with that of its published spectrum was identified as methylamine (84). Peak 1 corresponded to a published spectrum of carbon dioxide (m/e = 44). Peak 3 was too small to be identified. Peak 4 was identified as solvent, acetonitrile. Peak 5 was identified as dimethyldisulfide (55) by comparison of its mass spectrum to that of a published spectrum (85). Smaller peaks were not identified.

Photolysis of methomyl (8) in Acetonitrile with Hanovia lamp.

The photolysis of methomyl was carried out in a more concentrated acetonitrile solution (3.24 g, 0.02 mol, in 40 ml of acetonitrile). The same general procedure as above was used. The samples were irradiated with a Hanovia 450 watt high pressure mercury lamp for 6h. The gas chromatographic analysis with columns G and H at 50-110°C gave at least six peaks. By comparison of retention times with those of the different components in a standard solution and with mass spectra of authentic samples, the products were identified to be methylamine (m/e = 31), acetonitrile (solvent) dimethyldisulfide (m/e = 94) and the methylhydrazone of biacetyl (m/e = 142). Another product with m/e = 105, was identified to be the oxime of methomyl by comparison

with the mass spectrum of an authentic sample (86).

Photolysis of Methomyl in Tetrahydrofuran with λ=254 nm.

A solution of methomyl (3.24 g, 0.02 mol) in 100 ml of tetrahydrofuran was prepared and the general procedure used earlier was followed. Irradiation with Rayonet 254 nm lamps for varying times (50 min to 3.5h) gave the same peak sequence on analysis with column A at 60°, column B at 70°-180°C, and columns G and H at 55°-90°C. Analysis on column B at 70° gave 8 to 10 peaks. Using column F at 70°, peak 1 was identified as carbon dioxide. Peak 2 was identified as methylamine, a result reinforced by using column G at 35°. Its GC-MS spectrum was compared to that of a published spectrum. Peak 3 was identified as solvent. Peak 4 was identified as acetonitrile by comparing its GC-MS spectrum to that of an authentic sample (m/e = 41). Peak 5 with m/e = 58 was acetone, while peak 6 with m/e = 94 proved to be dimethyldisulfide. Two peaks with m/e = 78 and m/e = 79, respectively, were not identified. Peak 9 with m/e = 118 was assigned the molecular formula, $C_4H_{10}N_2S$ on the basis of GC-MS data. Peaks 10, 11, with m/e = 142 were identified as isomers of the methylhydrazone of biacetyl, $C_6H_{14}N_2$. Further analysis showed peak 11 was a dimer of tetrahydrofuran. By synthesizing the methylhydrazone of biacetyl and comparing its mass spectrum to the spectra obtained in GC-MS analysis, peak 10 proved to be the methylhydrazone of biacetyl (54).

Photolysis of Methomyl in Tetrahydrofuran with a Hanovia 450 watt Lamp.

A 50 ml solution of methomyl (0.138 g, 0.001 mol) in tetra-

hydrofuran was prepared. The sample was treated following the same general procedure already illustrated. Analysis using column E at 35°-100°C gave at least twelve peaks. In addition to peaks corresponding to methylamine, acetonitrile, dimethyldisulfide, biacetyl methylhydrazone, additional peaks proved to be due to dimethylamine (m/e = 45), N,N-dimethylurea, the thioketimine (64), dimethyl sulfoxide, methyl thioacetate (m/e = 90 compared to the mass spectrum of an authentic sample) and the oxime of methomyl (m/e = 105).

Photolysis in Other Solvents with λ=254 nm.

The photolyses of methomyl was also studied in methanol, ethanol, benzene and isopropanol. The same array of products was observed. In addition to products already identified, peaks with m/e = 84 and m/e = 86 could not be identified. A peak with m/e = 58 was identified as methylisocyanate. The peak with m/e = 84 could be cyclohexane being the result of photoreduction of benzene. The mass spectrum is an exact fit. The peak with m/e, 86 has a suggested structure based on mass spectral information to be $(CH_3)_2C\text{-}CH{=}NOH^+$.

Photolysis of Methomyl in Tetrahydrofuran with Benzonitrile Sensitizer.

A solution of methomyl (0.5 g, 0.003 mol) and benzonitrile (4.02 g, 0.04 mol) in 100 ml of tetrahydrofuran was prepared and irradiated with Rayonet 254 nm lamps using the general procedure illustrated above. When analysed using column B at 60° and column G at 55°C, products obtained were the same as those in the direct irradiation. The products were identified as methylamine (16%),

acetonitrile (45%), dimethyldisulfide (29%) and biacetyl methylhydrazone (5%).

Photolysis of Methomyl in Tetrahydrofuran with Benzophenone Sensitizer.

A solution of methomyl (0.499 g, 0.003 mol) and benzophenone (5.47 g, 0.03 mol) was prepared in 100 ml of tetrahydrofuran. Sample solutions in resealable quartz tubes were degassed and irradiated with Rayonet 300 nm lamps. Analysis using column B at 60° and column H showed that methylamine (32%), acetonitrile (30%), dimethyldisulfide (30%) and biacetyl methylhydrazone (7%) are the major procucts. The same array of products obtained with Rayonet 254 nm and the Hanovia 450 watt high pressure mercury lamp are used with an even greater number of peaks in the latter case. Acetophenone and benzophenone were chosen as they absorb at least 90% of the light at this wavelength.

Photolysis of Methomyl in Acetonitrile with Benzophenone.

A solution of methomyl (1.369 g, 0.009 mol) and benzophenone (1.7230 g, 0.010 mol) in 25 ml of acetonitrile was prepared, degassed and irradiated for 15h using Rayonet 254 nm lamps. Analysis on column H at 55° gave seven peaks. The main products obtained were methylamine, dimethylamine, acetonitrile (solvent) and dimethyldisulfide. Products were observed in slightly higher yields when compared to direct irradiation experiments. Reactions in acetonitrile were observed to be less efficient than reactions in tetrahydrofuran. The lower triplet energy sensitizers such as benzonitrile and acetophenone

gave the same array of products but in smaller yields.

Photolysis of Methomyl in Benzene with Sensitizers.

Methomyl solutions in benzene with benzophenone, acetophenone, and benzonitrile respectively were prepared and irradiated under varying conditions following the general procedure already illustrated. The only peaks identified were those corresponding to methylamine, acetonitrile and dimethyl disulfide.

Determination of Quantum Yields of Photoproducts of Methomyl.

Photoproduct quantum yields were determined on four 5 ml portions of methomyl (12.23 g, 0.50 M) in 200 ml of tetrahydrofuran. These and four 5 ml portions of the actinometer (cyclopentanone) in tetrahydrofuran were placed in resealable quartz tube, degassed by at least five freeze-thaw cycles and irradiated with Rayonet 254 nm lamps for 31h. Analyses were carried out by comparison of peak areas of the products relative that of a standard on an FID-GC with an integrator. All products were analyzed with column H at 55°C with isoamyl alcohol as internal standard. The actinometer was analyzed under the same conditions. Cyclopentanone forms 4-pentenal as the major product with a quantum yield of 0.37 at 300 nm, or 0.38 at 254 nm (87). Calculations done were based on the method of Calvert and Pitts (88). The results are summarized in Table I.

Quantum Yields of Photoproducts of Methomyl in Tetrahydrofuran With Benzophenone.

A 250 ml solution of methomyl (1.2535 g, 0.008 mol) and benzophenone (3.005 g, 0.016 mol) in tetrahydrofuran was prepared. Portions of 5 ml were placed in resealable quartz tubes, degassed and irradiated for 20h with Rayonet 254 nm lamps. Analysis using column H at 40°-110°C and peak areas obtained using a digital integrator gave the results summarized in Table II.

Quantum Yields of Photoproducts in the Irradiation of Methomyl in Tetrahydrofuran

Quantum yields of photoproducts of methomyl in tetrahydrofuran were determined according to the same general procedure above. Irradiation with a Hanovia 450 watt lamp for 6h showed a significant increase in quantum yields. Calculations of quantum yields were based on relative peak areas of products to that of isoamyl alcohol (internal standard). Results obtained are summarized in Table III.

Quantum Yields of Photoproducts of Methomyl in Acetonitrile, Benzene and Methanol.

A 25 ml solution of methomyl (1.565 g, 0.010 mol) and isoamyl alcohol (0.0695 g, 0.0008 mol) internal standard in acetonitrile was prepared. Samples of 5 ml each were placed in four resealable quartz tubes, degassed and irradiated for 15h with Rayonet 254 nm lamps. Analysis using column H at 50°-110°C with a GC-FID gave the results summarized in Table IV.

Quantum yields were also determined for the sensitized irradiation of methomyl (1.3855 g, 0.0085 mol) with benzophenone (3.264 g, 0.017 mol) in 25 ml of acetonitrile. Samples of 5 ml portions in

four resealable quartz tubes along with samples of the actinometer solution in acetonitrile were irradiated for 15h. The results obtained using column H at 50^{o}-110^{o}C are summarized in Table V.

Quantum yields were determined by the same general procedure used above for methomyl in benzene and methanol and are summarized in Table VI for methanol.

Quenching Effects on Methomyl Photoproduct Quantum Yields.

A 0.50 M standard solution of methomyl (16.23 g, 0.10 mol) and isoamyl alcohol (3.038 g, 0.035 mol) in 200 ml of tetrahydrofuran was prepared. A 2.596 M standard solution of isoprene (17.6825 g, 0.2596 mol) in tetrahydrofuran was prepared. Samples of 10 ml of the methomyl standard solution were introduced into 10 different 100 ml volumetric flasks. Varying amounts of the isoprene solution standard solution were then added to each of the volumetric flask and the volume of solution made up to 100 ml. Samples of the final solutions (5 ml portions) ranging in concentration from 2.6×10^{-2} M to 26.0×10^{-2} M were placed in sample tubes, degassed and irradiated with Rayonet 300 nm for 31h. This is approximately equivalent to a 90% conversion of methomyl in the absence of a quencher. The final solutions were 0.05 M in methomyl. An actinometer solution in tetrahydrofuran was prepared and photolyzed accordingly. Quenching quantum yields were determined by disappearance of starting material relative to isoamyl alcohol (internal standard). The quantum yields of photoproducts in absence of quencher were determined based on product formation in the sample that contained no quencher. Results are

summarized in Table VII.

Sample	Quencher Concentration
0	0.000 M quencher 0.5 M methomyl
1	2.6×10^{-2} M 0.5 M in methomyl
2	5.2×10^{-2}M 0.5 M in methomyl
3	7.8×10^{-2} M 0.05 M in methomyl
4	10.4×10^{-2} M 0.5 M in methomyl
5	12.0×10^{-2} M 0.05 M in methomyl
6	15.6×10^{-2} M 0.05 M in methomyl
7	18.2×10^{-2} M 0.05 M in methomyl
8	20.8×10^{-2} M 0.05 M in methomyl
9	23.4×10^{-2} M 0.05 M in methomyl
10	26.0×10^{-2} M 0.05 M in methomyl

Higher quencher concentration effects on quantum yields were also investigated and results are summarized in Table VIII. The corresponding Stern-Volmer plots of the ratio of quantum yields in absence and presence of quencher against varying quencher concentrations at low and high quencher concentrations are presented in Fig. 16 and 17.

Synthesis of Biacetyl Methylhydrazone.

Methylhydrazine (25 g, 0.544 mol) was dissolved in 130 ml of phototrex methanol contained in a 250 ml three-necked round bottom flask equipped with a dropping funnel, a magnetic stirrer, and a thermometer. The solution was maintained at 45°-50°C while a freshly distilled solution of biacetyl (5 g, 0.058 mol) in 100 ml of phototrex

methanol was added with stirring over a period of 2.5h. After addition was complete, stirring was continued at the same temperature for at least 5h. Excess solvent was removed by fractional distillation and the resulting solid was removed by filtration, washed with methanol and water, and then air-dried.

The yield of biacetyl methylhydrazone was 6.2 g (75%), m.p. 44°. The infrared spectrum neat showed absorptions at 3325 cm^{-1} (N-H, N-CH_3); 2850 cm^{-1} (CH_3-C=N); 1685 cm^{-1} (C=N-); NMR ($CDCl_3$, 100 MHz) δ1.9 (s, 6H), δ3.0 (s, 6HO and δ4.6 (2H); ^{13}C-NMR: δ9.00 ($\underline{C}H_3$-C=N), δ38 (N-$\underline{C}H_3$), δ144.8 (-C=N), MS, m/e 142 comparable to that obtained in photolyses experiments.

Anal: Calcd. for $C_6H_{14}N_2$: 50.68% C, 9.92% H, 39.40% N; Found: 50.01% C, 9.81% H, and 39.46% N.

This compound is reported to be somewhat volatile and evaporates at room temperature. In addition it loses weight easily and apparently undergoes air oxidation.

Photolysis of Biacetyl Methylhydrazone in Acetonitrile.

A 25 ml acetonitrile solution of freshly prepared biacetyl methylhydrazone (0.498 g, 0.004 mol) was prepared and irradiated for 9h with Rayonet 300 nm lamps. Analysis on column H at 55°C gave five peaks. Peak 1 was identified as methylamine (m/e, 31). Peak 2 is solvent (acetonitrile). Peak 3 was identified as methylhydrazone of acetaldehyde (m/e, 72). Peaks 4 (m/e, 142) and 5 were not identified. No yields were determined.

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