AN ABSTRACT OF THE THESIS OF

<u>Kermit C. McCarthy</u> for the degree of <u>Master of Science</u>

in <u>Chemistry (Organic)</u> presented on <u>August 31, 1978</u>

Title: <u>THE PHOTOCHEMISTRY OF SOME O-(METHYLCARBAMOYL)</u>

<u>OXIMES</u>

Abstract approved: Redacted for Privacy

Dr. Peter K. Freeman

The photochemistry of aldicarb and two related compounds,

O-(methylcarbamoyl) isobutyraldehyde oxime and O-(methyl-

carbamoyl) trimethylacetaldehyde oxime was explored under labora-

tory conditions. Upon irradiation aldicarb decomposed rapidly to

methylamine, dimethylamine, tetramethylsuccinonitrile, and

1-methylthio-2, 3-dicyano-2, 3-dimethylbutane. The other two

compounds decomposed only after a long period of irradiation. The

difference in reactivity was attributed to a photodesmotic interaction

between the sulfur and the imine double bond in aldicarb.

The Photochemistry of Some
O-(Methylcarbamoyl) Oximes

by

Kermit D. McCarthy

A THESIS

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Professor of Chemistry
         in charge of major

Redacted for Privacy

Chairman of the Department of Chemistry

Redacted for Privacy

Dean of Graduate School

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ACKNOWLEDGEMENTS

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O-(METHYLCARBAMOYL) OXIMES

INTRODUCTION

In 1969 1, 133, 377, 000 pounds of pesticides were produced and

poured into the environment (1). The eventual effect of these chemi-

cals upon the environment may be unknown and under natural condi-

tions many of these may be converted into products which also have

unknown effects. Sunlight above 2860 $\overset{\circ}{A}$ penetrates the ozone in the

atmosphere allowing photochemical reactions of the pesticides by

direct irradiation or through sensitization by other chemicals present

in the environment (2). This photodecomposition can produce chemi-

cals with undesirable ecological effects. The concern over this

problem led to the study of the photochemistry of several chlorinated

pesticides. The photoproducts of some of the pesticides studied were

found to be more toxic to mammals and fish than the original com-

pound (3). Upon irradiation aldrin(1) produces photoaldrin(2)

dieldrin(3) converts to photodieldrin(4) endrin(5) produces keto-

endrin(6) while heptachlor(7) forms photoheptachlor(8). These

photoproduces were all proven to be more harmful than their pre-

cursors (4). However, the photochemistry of many pesticides is

still unknown. Investigation must be carried out in the laboratory on

"realistic model systems" (4) to determine the outcome of over a

billion pounds of pesticides released into the environment each

year.
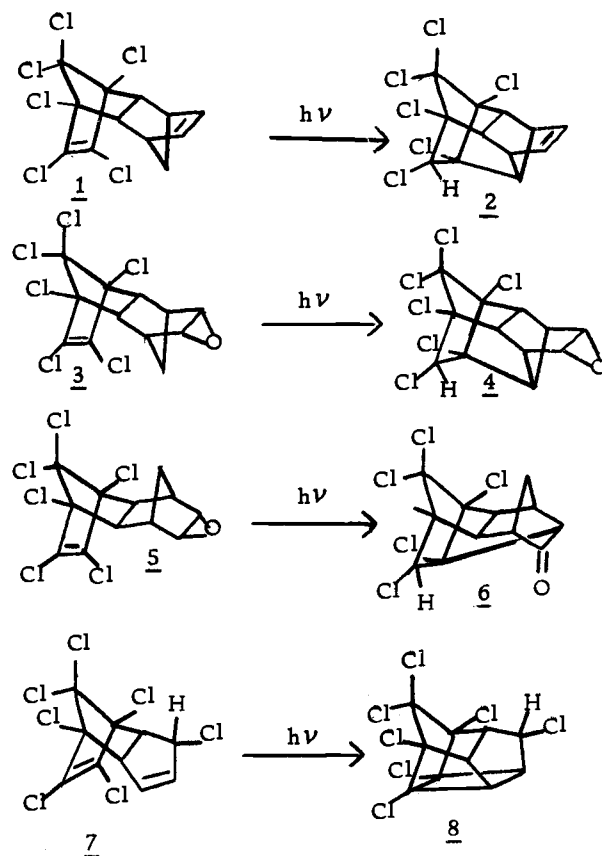
To increase the understanding of these outcomes the photo-

chemistry of the previously unstudied aldicarb and two related com-

pounds was studied under laboratory conditions. To provide a back-

ground for an investigation of the photochemistry of these compounds

it is necessary to review the synthesis, pesticidal activity, general

chemistry, metabolism, analysis, and photochemistry of relevant

substrates.

Synthesis

The synthesis of aldicarb was first reported by Payne in 1966

(5). He synthesized a large series of compounds using the following

sequence. A chloronitroso dimer 9 was heated to form a chloro-

oxime 10. This underwent nucleophilic attack to yield the appropriate

oxime 11. The oxime 11 was then treated with methylisocyanate with

an amine catalyst to yield the expected product 12. In 1966 Bartley

used essentially the same synthesis to produce aldicarb labelled

with C_{14} in three positions (6). C_1 labelled tertiary butyl alcohol(13)

was dehydrated on alumina at 300° to yield isobytylene(14). Isobutyl-

ene was treated with nitrosochloride to yield the nitrosochloro com-

pound 15 Payne used. Bartley then used Payne's sequence. Heating

the nonlabelled nitrosochloro compound with labelled sodium thio-

methoxide gave methylthio labelled aldicarb. Reaction of the non-

labelled oxime with methyl labelled methylisocyanate produced

methylamino labelled aldicarb.

$$[\,Cl\text{-}CR_2\text{-}CRH\text{-}NO]_2 \xrightarrow{\;\triangle\;} Cl\text{-}CR_2\text{-}\underset{R}{C}\text{=}NOH$$

$$\underline{9} \qquad\qquad \underline{10} \qquad \Big\downarrow \; NaX$$

$$X\text{-}CR_2\text{-}\underset{R}{C}\text{=}NO\overset{O}{\overset{\|}{C}}\,NHCH_3 \;\longleftarrow\; X\text{-}CR_2\text{-}\underset{R}{C} = N\,OH$$

$$\underline{12} \qquad\qquad\qquad \underline{11}$$

$$(CH_3)_3 \overset{*}{C}-OH \rightarrow (CH_3)_2 \overset{*}{C}=CH_2 \rightarrow [Cl-\overset{*}{C}(CH_3)_2 CH_2NO]_2$$

$$\underline{13} \qquad\qquad \underline{14} \qquad\qquad \underline{15} \quad \Big\downarrow \begin{array}{l} 1)\ \triangle \\ 2)\ CH_3\text{-}S^{\,-}\ Na^{\,+} \end{array}$$

$$CH_3\text{-}S\text{-}\overset{*}{C}(CH_3)_2 CH=NO\overset{\overset{O}{\|}}{C}NHCH_3 \xleftarrow{\quad CH_3NCO \quad} CH_3\text{-}S\text{-}C(CH_3)_2 CH{=}NOH$$
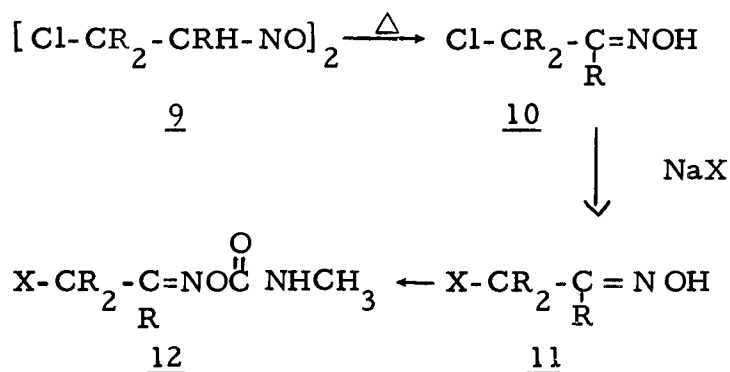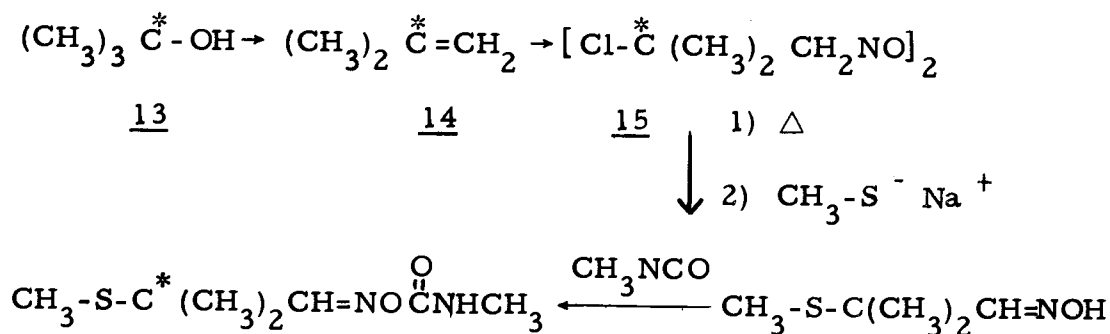
Several compounds related to aldicarb have been produced through a variety of methods. O-acyl oximes can be formed using many different techniques. The reaction of the oxime with acetic anhydride produces the desired product (eq. 1) (7, 8). Benzoyl chlorides add to oximes to yield benzoyl oximes (eq. 2) (9). N-phenyl oxime carbamates are readily formed by treating the oxime with phenyl isocyanate (eq. 3, 4) (10, or 11) alternatively through a reaction of the oxime with N, N-diphenylchloroformamide (eq. 5) (12). Another approach was used by Loev. In 1963 he reported the synthesis of O-carbamoyl oximes by allowing the oxime to react with cyanic acid formed _in situ_ from sodium cyanate and trifluoroacetic acid (eq. 6) (13).

$$(CH_3)_2C{=}NOH + (CH_3CO)_2\text{-}O \rightarrow (CH_3)_2\ C{=}NO\overset{\overset{O}{\|}}{C}CH_3 \qquad\qquad (eq.\ 1)$$

$$RCH{=}NOH + \phi COCl \rightarrow RCH{=}NO\overset{\overset{O}{\|}}{C}\phi \qquad\qquad (eq.\ 2)$$

$$\phi CH{=}NOH + Na \rightarrow \phi CH{=}NO^{\ominus}\ Na^{\oplus} \qquad\qquad (eq.\ 3)$$

$$\Big\downarrow \phi NCO$$

$$\phi CH{=}NOCONH\phi$$

$$RCH=NOH + \phi NCO \rightarrow RCH=NOCONH\phi \qquad \text{(eq. 4)}$$

$$RCH=NO^{\ominus}Na^{\oplus} + ClCON\phi_2 \rightarrow RC=NOCON\phi_2 \qquad \text{(eq. 5)}$$

$$CF_3COOH + NaOCN + R_2C=NOH \rightarrow R_2C=NO\overset{O}{\overset{\|}{C}}NH_2 \qquad \text{(eq. 6)}$$
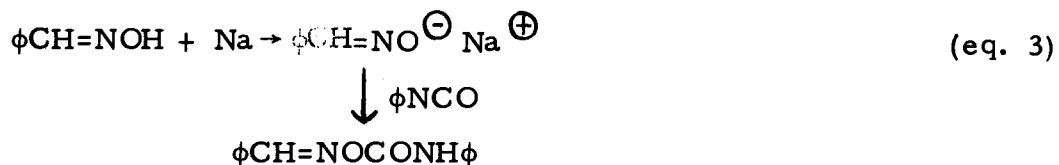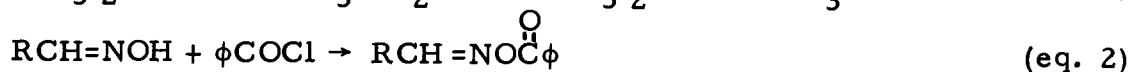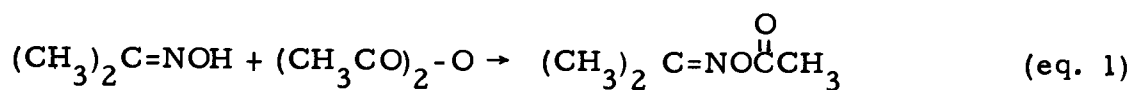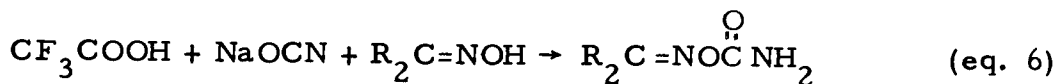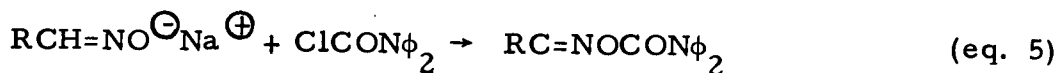
Pesticidal Activity
_____

In 1965 Weiden first reported the use of oxime groups in pesti-

cides. He specifically reported on O-(methylcarbamoyl)-3-chloro-6-

cyano-2-norbornanone oxime(16) and O-(methylcarbamoyl)-2-methyl-

2-methylthiopropanal oxime (aldicarb) (17). He found aldicarb to be

an effective pesticide for bean aphids, house flies, Mexican bean

bettles, boll weevils, and to have an LD_{50} of 1 mg/kg in rats (14).
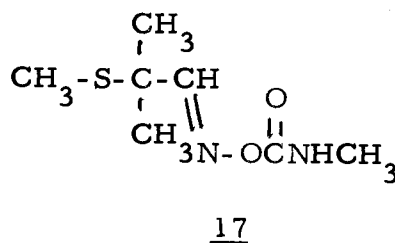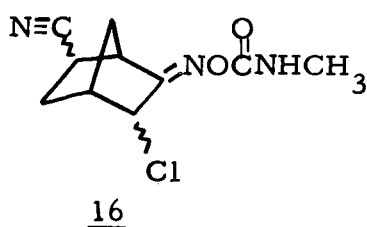
These pesticides are acetylcholinesterase inhibitors (5, 15).

Acetyl cholinesterase is an important enzyme in the nerve synapse.

It cleaves acetyl choline (18) to acetic acid (19) and choline (20). As

a result of a nerve impulse these recombine to form acetyl choline.

The acetyl choline formed reacts with a receptor protein triggering

formation of more acetyl choline and the impulse is passed down the

nerve. The acetyl cholinesterase hydrolyzes the acetyl choline to the starting materials after the signal is passed, shutting down the impulse (Scheme I). The pesticides kill the insects through competitive inhibition of the acetyl cholinesterase. They displace the acetyl choline at the enzyme's active site. The nerve impulse cannot shut off so the circuit is left on. The physiological effects are increased and erratic heart beat and in severe cases, cardiac arrest.

$$CH_3COOH + HOCH_2CH_2 \overset{\oplus}{N}(CH_3)_3 \rightarrow CH_3COOCH_2CH_2 \overset{\oplus}{N}(CH_3)_3$$

19   20   18

hydrolysis by   transmission
acetyl cholinesterase   of signal
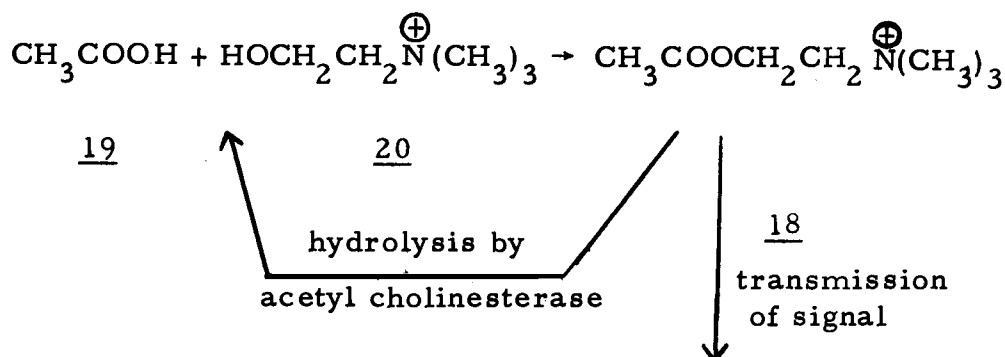
Scheme I

(16)

For the pesticide to compete successfully with the acetyl choline it has to meet several structural requirements. A substantial amount of work has been done to describe these requirements. The enzyme binds the acetyl choline at two sites. The carbonyl of the acetyl choline is bound to the enzyme by nucleophilic attack by a basic nitrogen (imidazole or oxazoline of the peptide sequences glycyl-aspartyl-glycine). Approximately 5.9 Å away is an anionic site on the enzyme (probably a $COO^{\ominus}$ group of aspartic or glutamic acid) which attracts the positively charged nitrogen of the acetyl choline (5).

This site is shaped to accommodate two methyl groups (15).

For a pesticide to be effective it has to meet these structural requirements. Metcalf tested a large assortment of compounds to determine the relationship between structure and competitive inhibition of the enzyme. The rate of ester hydrolysis is dependent on chain length and configuration of both alcohol and acid portions. Hydrolysis increases with alcohol chain length up to five carbons and then decreases. It increases with branching of four and five carbon chains of the alcohol. It decreases with increasing length of the acid portion. In fly brain the maximally hydrolyzed ester was 3, 3-dimethylbutyl acetate which was hydrolyzed 0.83 times as fast as acetyl choline (15).

If structural requirements were the only considerations, acetyl choline would be the best pesticide. But the positively charged nitrogen keeps it from penetrating the lipid nerve sheath and reaching the enzymatic site. To be effective as a pesticide, a compound needs to be polar enough to be accepted by the enzyme, but nonpolar enough to penetrate the lipid layers of the nerve sheath. Payne tried a wide range of possibilities. O-(methylcarbamoyl) trimethylacetaldehyde oxime gave good results with LD_{50} of 10 mg/kg for bean aphids and 30 mg/kg for house flies. It has a carbonyl 5.6 Å from a quaternary carbon which should allow for a good fit with the enzyme. The quaternary site is nonpolar which allows the compound to penetrate the nerve sheath. However, trading one of the methyls attached to

the quaternary carbon as in O-(methylcarbamoyl)-2-methyl-2-

methylthiopropanal oxime (aldicarb) gives even better results. The

LD_{50} for aphids is 4 mg/kg, house flies 4 mg/kg and rats 1 mg/kg.

Aldicarb and its sulfoxide appear to be the optimum inhibitors (5).

Aldicarb has widespread applicability as a pesticide. It has

been found to be effective for house flies, forth instar larvae, boll

weevil, bullworms, tobacco budworms (18), bean aphids, two spotted

mites, and Mexican bed beetles (5) among others.

General Chemistry

In the laboratory O-alkyl or O-aroyl oximes generally undergo

hydrolysis to produce oximes, nitriles, or isomerize from Z to E

and E to Z isomers. An (E) O-aroyl oxime under mild hydrolysis

conditions yields an (E) oxime and a (Z) O-aroyl oxime yields a

nitrile (eq. 7). Under mildly acidic conditions (E) oximes isomerize

to (Z) oximes (eq. 8) (9). As in the preceding, (E) O-carbamoyl

oximes under mildly basic conditions give oximes. Strongly basic

conditions produce nitriles (eq. 9). (Z) O-carbamoyl oximes give

nitriles under mildly basic conditions (eq. 10) (12). Benger theorized

the hydrogen is protected by the carbonyl hindering attack by the base.

Oxime formation is the result (19). Also the (E) oxime is properly

arranged for an antiperiplanar transition state. This is analogous

to the base induced elimination in cis and trans β bromo-styrene.

Elimination from the <u>cis</u> styrene is significantly faster than elimination from the <u>trans</u> styrene. The increased elimination rate is attributed to a concerted hydrogen abstraction and bromine elimination step (E2). The geometry in the <u>cis</u> case is appropriate for an antiperiplanar transition state while the <u>trans</u> bromo-styrene has to undergo a multi-step carbanion mechanism (20).

$$\underset{\phi COO-N}{\overset{RCH}{\parallel}} \xrightarrow{\text{pyr}} RCN \quad \underset{NOOC\phi}{\overset{RCH}{\parallel}} \xrightarrow{\text{pyr}} \underset{NOH}{\overset{RCH}{\parallel}} \qquad \text{(eq. 7)}$$

$$\underset{Z}{} \qquad\qquad\qquad \underset{E}{}$$

$$\underset{\phi COON}{\overset{RCH}{\parallel}} \underset{\longleftarrow}{\longrightarrow} \underset{NOOC\phi}{\overset{RCH}{\parallel}} \qquad\qquad \text{(eq. 8)}$$

$$\underset{Z}{} \quad\quad \underset{E}{}$$

$$\underset{NOOCN\phi_2}{\overset{RCH}{\parallel}} \xrightarrow{\text{n-buNH}_2} \underset{NOH}{\overset{RCH}{\parallel}} \qquad \text{(eq. 9)}$$

$$\xrightarrow[]{\text{Hot NaOH}} RCN$$

$$\underset{R_2NCOON}{\overset{RCH}{\parallel}} \xrightarrow[\text{NaOH}]{\text{Cold}} RCN \qquad \text{(eq. 10)}$$

21   22
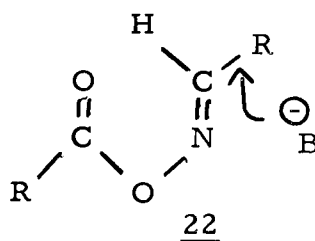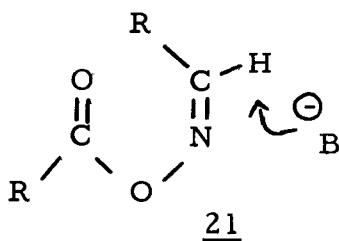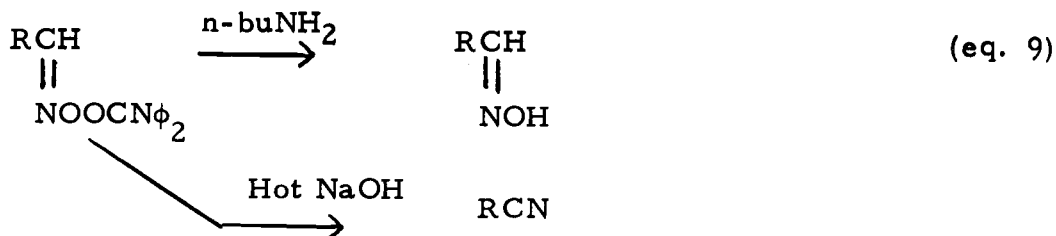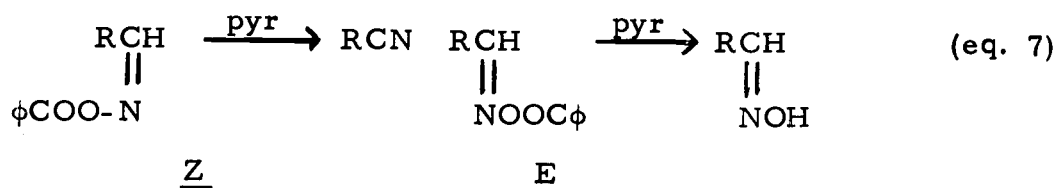
Aldicarb undergoes three basic reactions; hydrolysis, oxidation, and elimination. When treated with base aldicarb hydrolyzes to the oxime (eq. 11) (5, 17). Since the oxime is the product of hydrolysis aldicarb (17) must be the (E) oxime, as would be expected from steric considerations. Oxidation of the sulfur takes place very readily. Aldicarb treated with hydrogen peroxide gives either the sulfoxide or the sulfone depending on the duration of the reaction (eq. 12) (17). Thermal decomposition of aldicarb yields the nitrile through a cyclic mechanism (eq. 13) (5). This mechanism is similar to that of ester pyrolysis involving a six membered transition state (eq. 14) (21).

$$CH_3-S-C(CH_3)_2CH=NOCOONHCH_3 \xrightarrow{\text{Base}}$$

$$CH_3-S-C(CH_3)_2CH=NOH \qquad \text{(eq. 11)}$$

$$CH_3-SC(CH_3)_2CH=NOCOONHCH_3 \xrightarrow{H_2O_2}$$

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{S}-C(CH_3)_2CH=NOCO-NHCH_3 \qquad \text{(eq. 12)}$$

$$CH_3-S-C(CH_3)_2 \; C\overset{H}{\underset{N-O}{\diagdown}}\overset{O}{\diagup}C-NHCH_3 \xrightarrow{\Delta}$$

$$CH_3-S-C(CH_3)_2C\equiv N \qquad \text{(eq. 13)}$$

$$R_2C-\underset{R_2}{C}\overset{\overset{\displaystyle R}{\diagdown}C=O}{\diagup}H \longrightarrow R_2C=CR_2 \qquad \text{(eq. 14)}$$
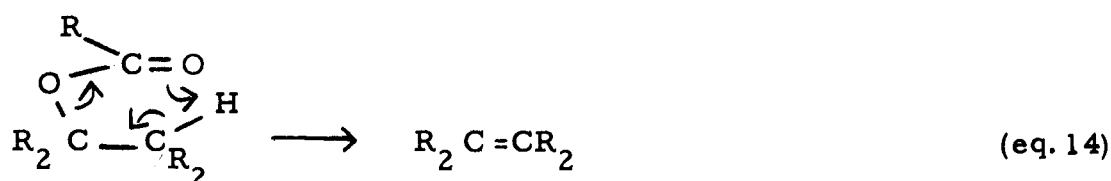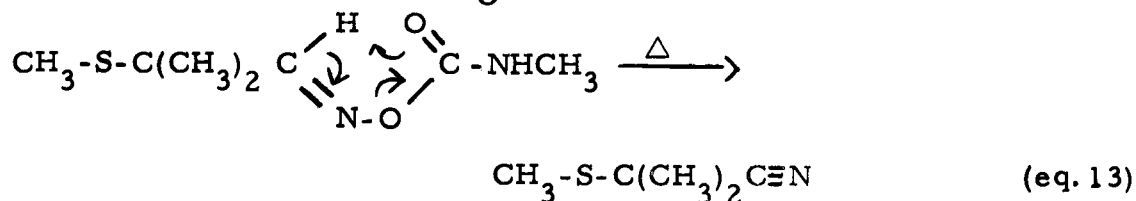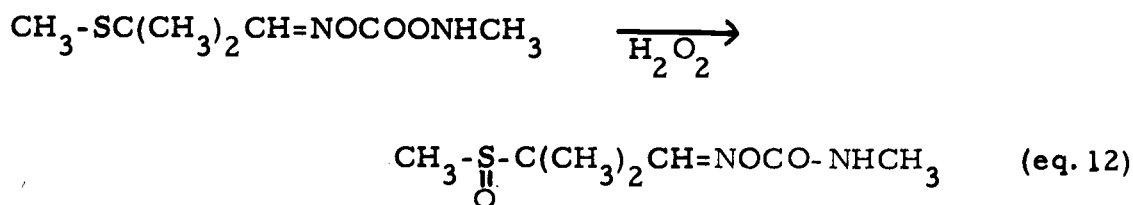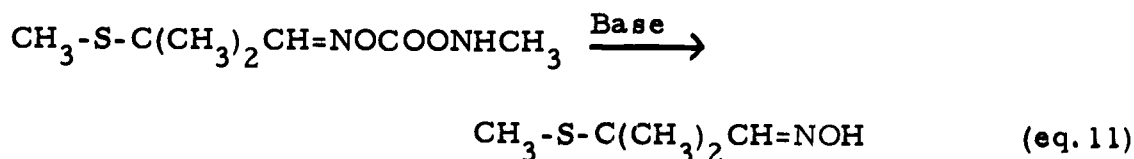
Metabolism

Aldicarb's metabolic decomposition proceeds via two pathways; hydrolysis and oxidation. Oxidation of aldicarb to the sulfoxide is rapid in cotton plants (22, 23), soil (22, 24), potato plants (25), cows (26), internally in insects (18), rats (27), and sugar beets (28). Further oxidation to the sulfone takes place much more slowly. Hydrolysis to the oxime or oxime sulfoxide also takes place in the above conditions, but it also is slow. The general pattern of metabolic breakdown is illustrated in Scheme II.

The half life of aldicarb varies from 24 hours to 7 days depending on the conditions. The half life of aldicarb sulfoxide ranges from 14 days to 28 days. The rapid oxidation of aldicarb to the sulfoxide and the sulfoxide's relative stability is important. The sulfoxide is also fairly toxic (LD_{50} for rats 1 mg/kg, bean aphids 3 mg/kg, two spotted mites 15 mg/kg and house flies 5 mg/kg (5)) and adds appreciably to aldicarb's use as a pesticide.

$$CH_3-S \ C(CH_3)_2 \ CH_3)_2 \ CH=NO\overset{\overset{O}{\parallel}}{C}NHCH_3 \quad \xrightarrow{\text{rapid}} \quad CH_3-S\overset{\overset{O}{\parallel}}{C}(CH_3)_2CH=NO\overset{\overset{O}{\parallel}}{C}NHCH_3$$

slow ↓   rapid ↓   slow ↓

$$CH_3-S-C(CH_3)_2 \ CH=NOH \qquad CH_3-S\overset{\overset{O}{\parallel}}{C}(CH_3)_2 \ CH=NOH$$

$$[CH_3-S-\overset{\overset{O}{\parallel}}{C}(CH_3)_2CH=O] \qquad CH_3-S\overset{\overset{O}{\parallel}}{C}(CH_3)_2C\equiv N \qquad CH_3-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}-C(CH_3)_2 \ CH=NO\overset{\overset{O}{\parallel}}{C}NHCH_3$$

$$CH_3-\overset{\overset{O}{\parallel}}{S}-C(CH_3)_2CH_2OH \qquad\qquad CH_3-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}C(CH_3)_2CH=NOH$$

$$CH_3-\overset{\overset{O}{\parallel}}{S}C(CH_3)_2\overset{\overset{O}{\parallel}}{C}NH_2 \qquad [CH_3-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}C(CH_3)_2CH=O]$$

$$CH_3-\overset{\overset{O}{\parallel}}{S}C(CH_3)_2\overset{\overset{O}{\parallel}}{C}OH \qquad CH_3-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}C(CH_3)_2 \ CH_2OH$$

$$CH_3-\overset{\overset{O}{\parallel}}{\underset{\parallel}{S}}-C(CH_3)_2 \ \overset{\overset{O}{\parallel}}{C}OH$$
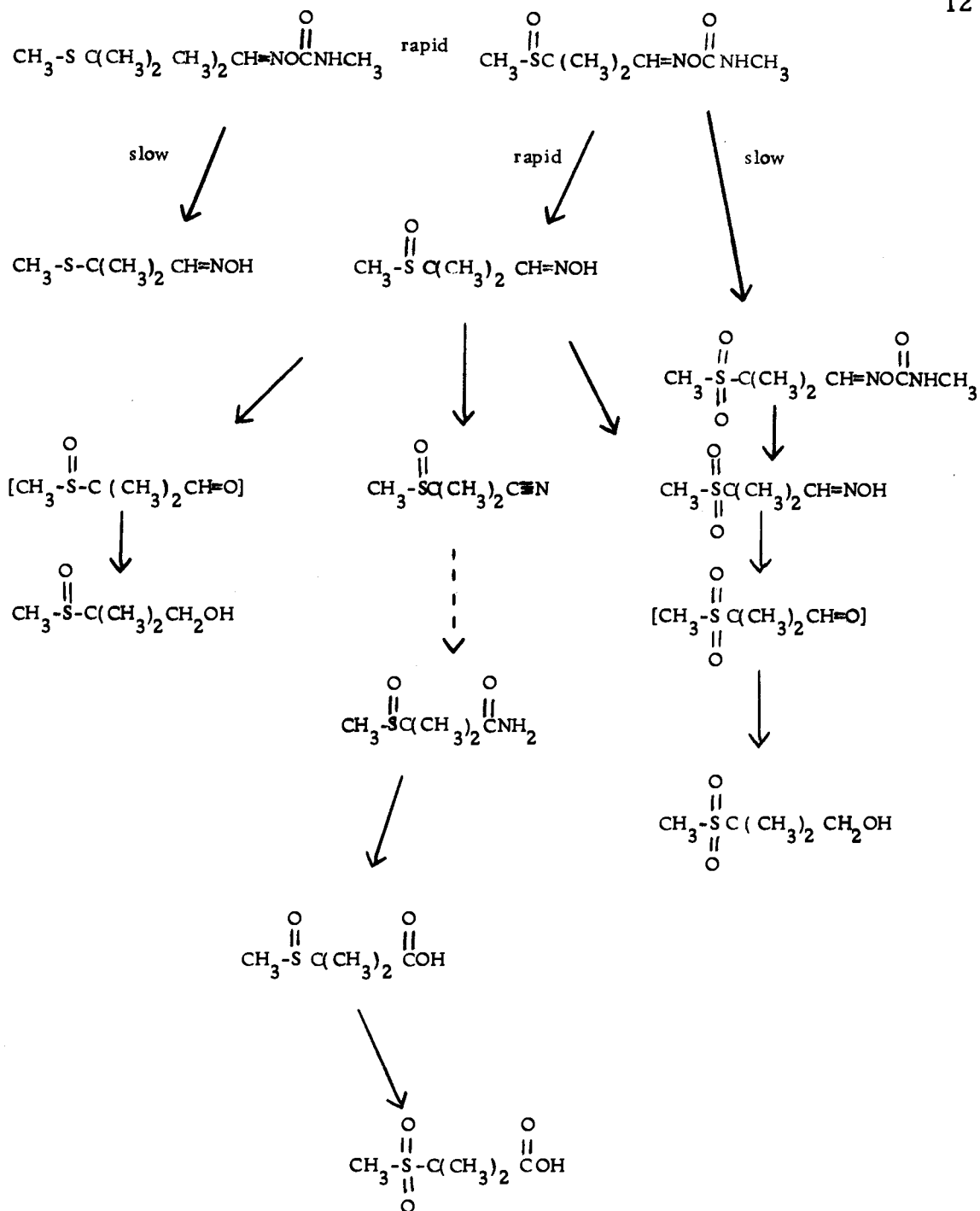
Scheme II

The metabolic decomposition of aldicarb in potato tubers seems to vary from the above pathway. Hydrolysis is much more rapid relative to oxidation and the oxime of aldicarb is an important metabolite (Scheme III). Evidently, the oxidation of the sulfur portion takes place more rapidly in the photosynthetic parts of the plant (25).

$$CH_3-S-C(CH_3)_2CH=NOCNHCH_3 \xrightarrow{\text{rapid}} CH_3-S-C(CH_3)_2CH=NOH$$

$$\downarrow \text{slow}$$

$$CH_3-SO-C(CH_3)_2CH=NOCNHCH_3 \xrightarrow{\text{rapid}} CH_3-SOC(CH_3)_2CH=NOH$$

$$\downarrow \text{slow}$$

$$CH_3-SO_2C(CH_3)_2CH=NOCNHCH_3$$
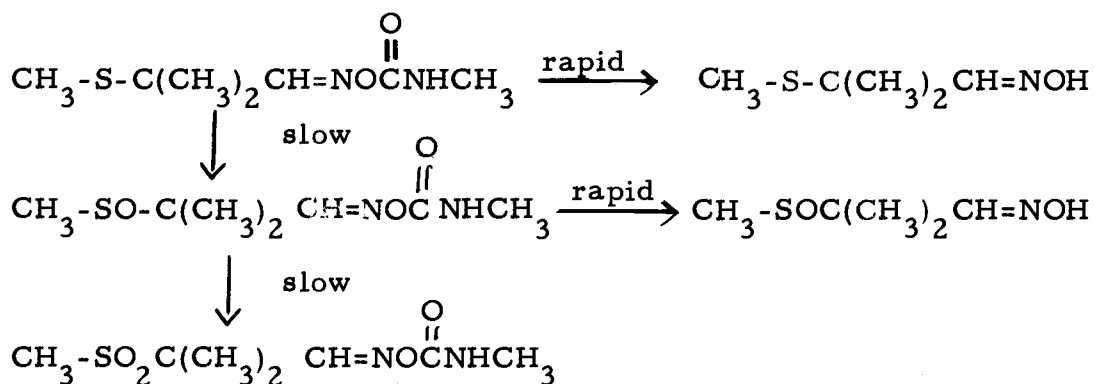
Scheme III

Analytical

A variety of analytical methods have been developed for quantifying aldicarb in the environment. In 1966 Johnson developed an elaborate scheme for colorimetric determination of aldicarb. Aldicarb was hydrolyzed with acid to the aldehyde and hydroxylamine. The hydroxylamine was treated with sulfanilic acid to give a diazonium salt. The salt was treated with 1-naphthylamine to give a colored product (29).
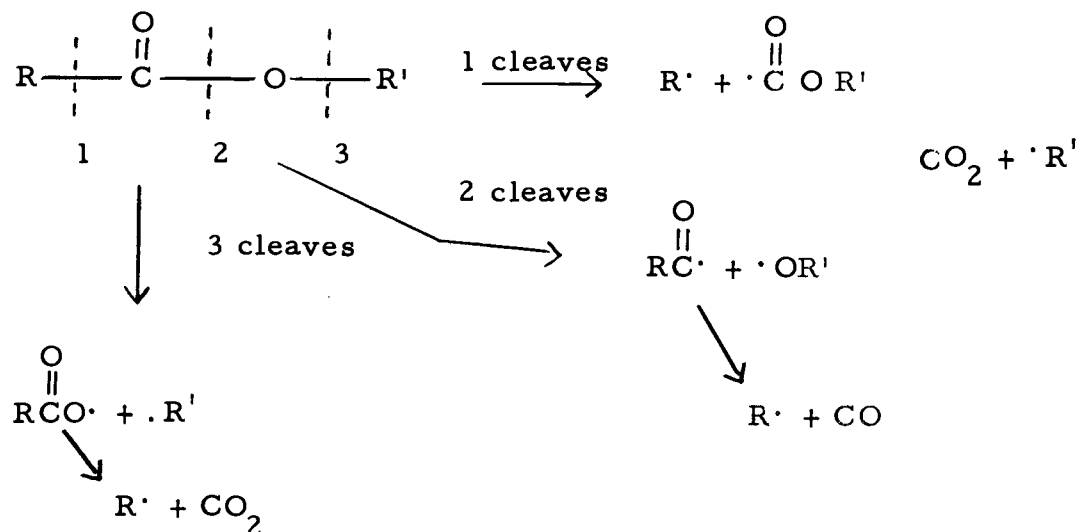
A variety of chromatographic techniques have been used in analyzing for aldicarb. Two-dimensional thin layer chromatography using several different solvent systems was used by Coppedge (22).

Knaak employed a silica gel column with 1 to 1 dioxane-isooctane (27).

Aldicarb decomposes to the nitrile on a 4' x 4 mm ID glass 10% DEGS

80/100 Gas Chrom Q and can be quantified with a FID detector (30).

Maitlen used a 122 cm x .175 cm ID steel or aluminum 5% Carbowax

20M + 10% DC 200 on 60/80 Gas Chrom Q column with a FID detector

to determine aldicarb quantitatively as the sulfoxide. Several people

have determined aldicarb directly by gas chromatography (31). Bache

used a 2' x 3/16" ID glass 10% OV17 on 80/100 Gas Chrom Q column

with microwave powered helium omission and electron affinity detec-

tors (32). Beckman used a 5" x 6 mm OD glass 5% CW 20M + 10%

SE30 on 100/120 Gas Chrom Q column with microcoulometric detec-

tor (28). Recently Sparacino employed high pressure liquid chro-

matography for detection of aldicarb using a variety of columns and

solvent systems (33).

Photochemistry

Aldicarb contains several functional groups. Possible photo-

chemistry could involve any one or all of the functional groups. One

convenient analog to aldicarb is an ester. The three possible bond

cleavages have been observed when esters are irradiated (Scheme IV).

Further reactions can take place with these radicals to yield a large

assortment of products (34). If a β hydrogen is present in the alcohol

portion of the ester or a γ hydrogen in the acid portion a "Norrish

type II" reaction may take place (35) (Scheme V).

$$R \overset{O}{\underset{\|}{\vdash}} C \overset{\|}{\vdash} O \overset{\|}{\vdash} R' \xrightarrow{\text{1 cleaves}} R\cdot + \cdot \overset{O}{\underset{\|}{C}} O R'$$

$$1 \quad 2 \quad 3$$

$$CO_2 + \cdot R'$$

1 ↓

2 cleaves →

3 cleaves →

$$\overset{O}{\underset{\|}{RC}}\cdot + \cdot OR'$$

$$\overset{O}{\underset{\|}{RCO}}\cdot + .R'$$

$$R\cdot + CO$$

$$R\cdot + CO_2$$

Scheme IV

$$R_2CHCR_2O\overset{O}{\underset{\|}{C}}CR_2CR_2CHR_2 \xrightarrow{\gamma H} R_2CHCR_2O\overset{OH}{\underset{|}{C}}=CR_2$$

$$\downarrow \beta H$$

$$+ CR_2=CR_2$$
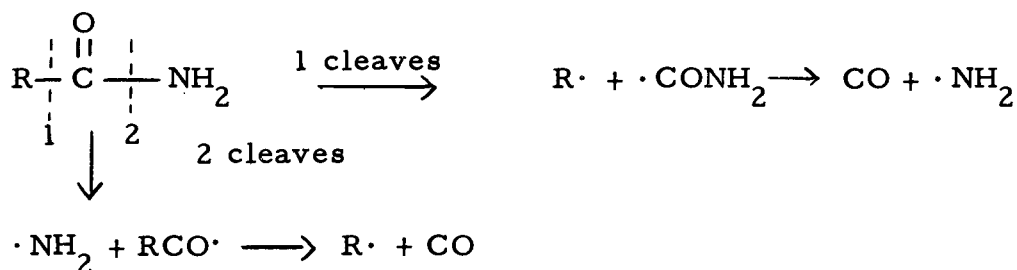
$$R_2C=CR_2 + HO\overset{O}{\underset{\|}{C}}CR_2CR_2CHR_2$$
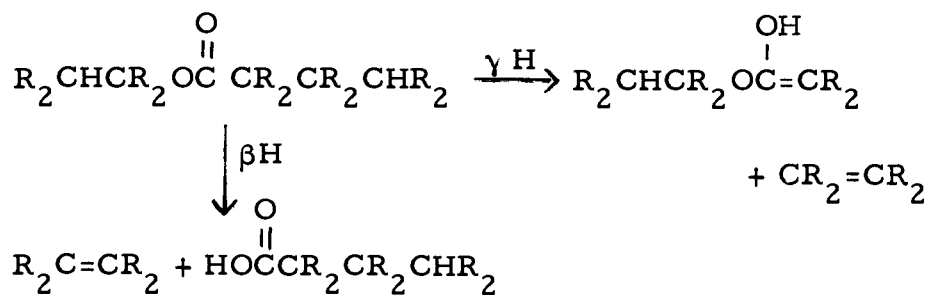
Scheme V

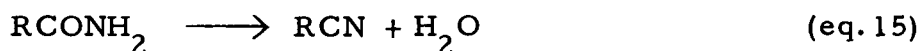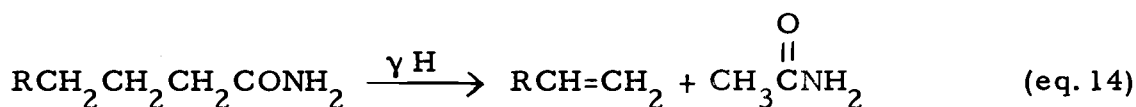Amides undergo photochemical reactions. Generally free radical formation takes place by cleavage of a carbon-carbon or a carbon-nitrogen bond (Scheme VI). Both processes yield the same radicals. The radicals may combine or undergo hydrogen abstraction to yield a variety of products. A "Norrish type II" reaction is also possible with amides if a γ hydrogen is present (eq. 14) (36). Simple

amides undergo dehydration upon irradiation (eq. 15).

$$R{-}\overset{\overset{O}{\|}}{C}{-}NH_2 \xrightarrow{\text{1 cleaves}} R\cdot + \cdot CONH_2 \longrightarrow CO + \cdot NH_2$$

$$\xrightarrow{\text{2 cleaves}}$$

$$\cdot NH_2 + RCO\cdot \longrightarrow R\cdot + CO$$

Scheme VI

$$RCH_2CH_2CH_2CONH_2 \xrightarrow{\gamma H} RCH{=}CH_2 + CH_3\overset{\overset{O}{\|}}{C}NH_2 \qquad \text{(eq. 14)}$$

$$RCONH_2 \longrightarrow RCN + H_2O \qquad \text{(eq. 15)}$$

The sulfide linkage present in aldicarb is another site of possible photochemical reaction. Photolysis of sulfides usually yields radicals which can abstract hydrogens or recombine to form almost any possible combination (eq. 16) (37).

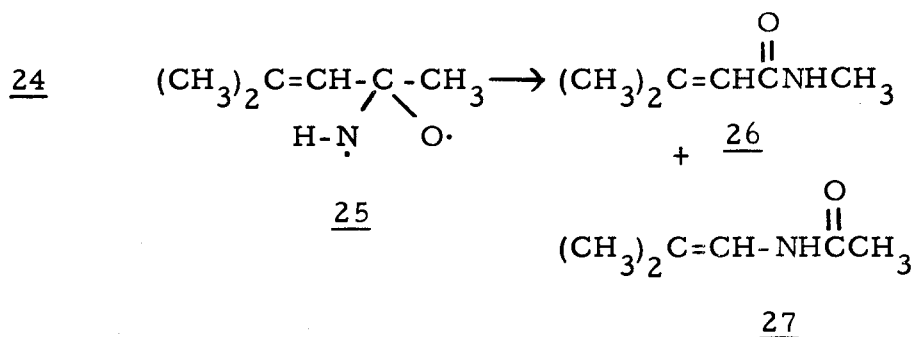$$RSR \longrightarrow R\cdot + \cdot SR \qquad \text{(eq. 16)}$$

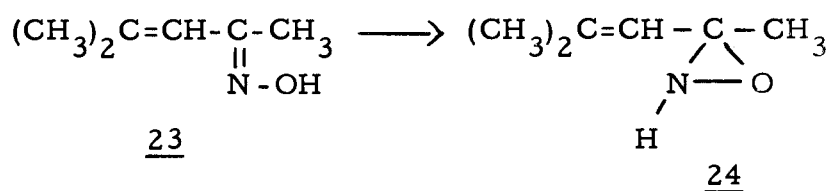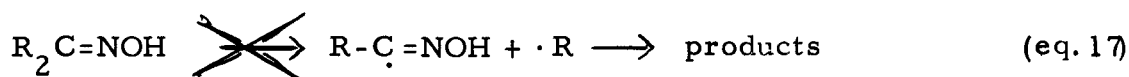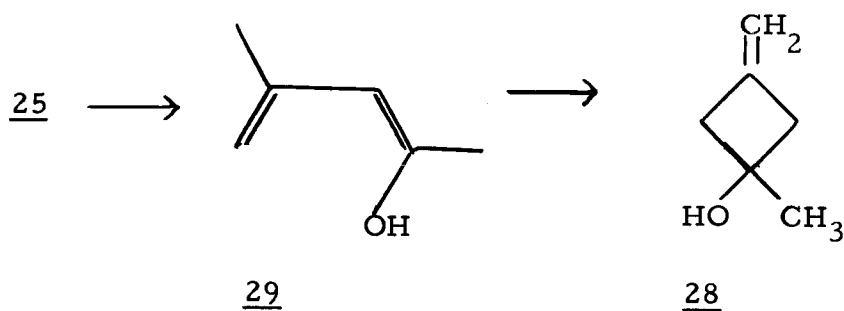Another important functionality of aldicarb is the oxime portion. Photochemically oximes undergo Beckmann rearrangement, hydrolysis to ketones, Z - E isomerization, and amide formation.

Photochemical Beckmann rearrangement products from oximes have been reported in several cases. Taylor reported irradiating cyclohexanone oxime to yield 46% lactam in methanol (expected Beckmann rearrangement product) (38). In 1968 Just photolyzed a
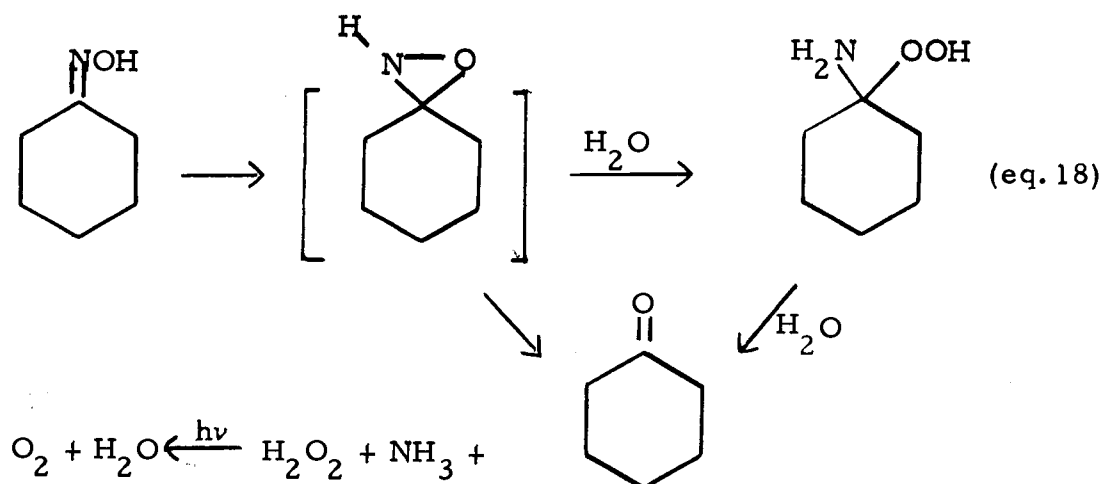
series of cyclic oximes from a four to twelve carbon ring. He re-
ported lactam formation in all cases, but with yields of less than 1%
(39). Sato reported photolysis of mesityloxide oxime (23) in methanol
giving Beckmann rearrangement products in 30% yield. He proposed
a mechanism using an oxaziridine 24 as an intermediate and not
rearrangement through "Norrish type I" cleavage (eq. 17). The
oxaziridine 24 may form the Beckmann rearranged products by
homolytic cleavage of the nitrogen-oxygen bond to form the diradical
25. This may rearrange to form 26 or 27. Evidence for this
mechanism was the presence of 28 as a product. The oxaziridine
24 could rearrange by cleaving to the diradical 25. This can undergo
intramolecular hydrogen abstraction through a cyclic transition state
to form the dienol 29. This can rearrange to 28 (40).

$$R_2C=NOH \quad \overset{\times}{\longrightarrow} \quad R-\underset{\cdot}{C}=NOH + \cdot R \longrightarrow \text{products} \qquad (\text{eq. }17)$$

$$(CH_3)_2C=CH-\underset{\underset{N-OH}{\overset{||}{}}}{C}-CH_3 \longrightarrow (CH_3)_2C=CH-\underset{\underset{H}{\overset{/}{N}\!\!-\!\!O}}{\overset{/}{C}\!\!\diagdown}-CH_3$$

$$\underline{23} \qquad\qquad\qquad \underline{24}$$

$$\underline{24} \quad (CH_3)_2C=CH-\underset{\underset{H-\underset{\cdot}{N}}{\overset{/}{}\diagup\diagdown\overset{}{O\cdot}}}{C}-CH_3 \longrightarrow (CH_3)_2C=CH\overset{\overset{O}{||}}{C}NHCH_3$$

$$\qquad\qquad\qquad\qquad\qquad + \quad \underline{26}$$

$$\underline{25}$$

$$(CH_3)_2C=CH-NH\overset{\overset{O}{||}}{C}CH_3$$

$$\underline{27}$$

25 ⟶ [structure 29]   ⟶   [structure 28]

29

28

Ketone formation is another possible photochemical process.

Taylor reported formation of cyclohexanone upon photolysis of the

oxime (38). In 1972 Sato reported that the irradiation of mesityloxide

oxime yielded ketones (40). Just reported formation of ketones in

yields ranging from less than one percent to six percent in a series

of cyclic oximes. He proposed a mechanism that required water and

used an oxaziridine as the intermediate (eq. 18) (39).

[reaction scheme showing cyclohexanone oxime → oxaziridine intermediate → with H_2O → H_2N, OOH substituted cyclohexane]   (eq. 18)

$$O_2 + H_2O \xleftarrow{h\nu} H_2O_2 + NH_3 +$$ [cyclohexanone structure] $\xleftarrow{H_2O}$

The ketones could also be formed directly from the oxaziridine inter-

mediate by expulsion of a nitrene.

The photolysis of oxime also yields amides. Taylor reported

formation of capramide in 5% yield in methanol and 52% in isopropyl

alcohol upon photolysis of cyclohexanone oxime (38). Just reported

amide formation in yields ranging from 3 to 50% upon photolysis of

a series of cyclic oximes. He gave a mechanism involving isopropyl

alcohol and the oxaziridine intermediate (eq. 19). This mechanism

was found to be consistent with deuterium labelling using deuteriated
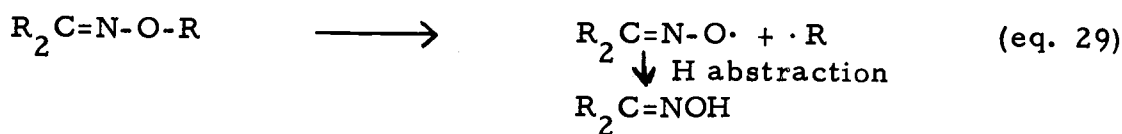
isopropyl alcohol (39).

(eq. 19)
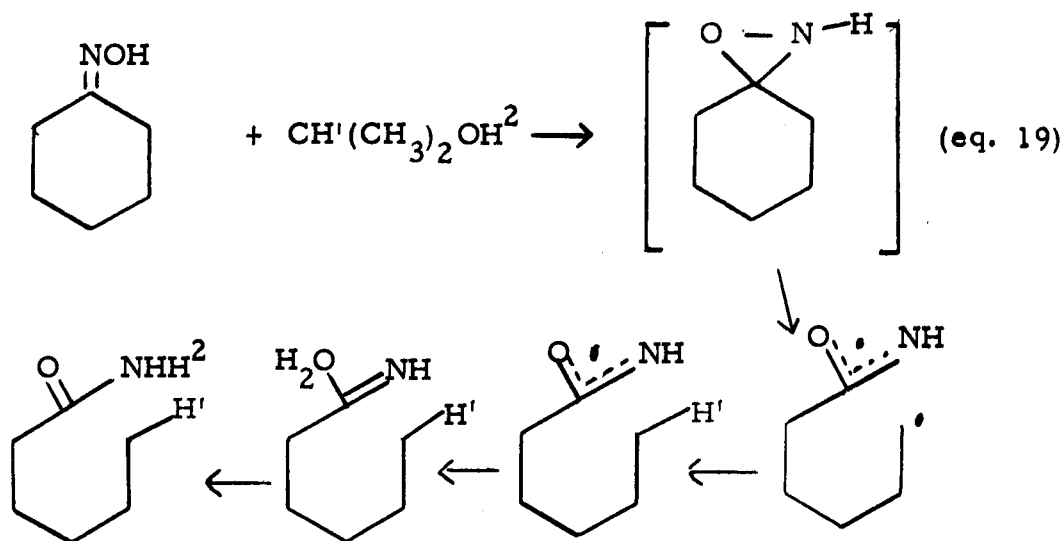
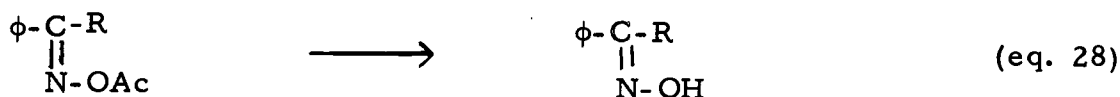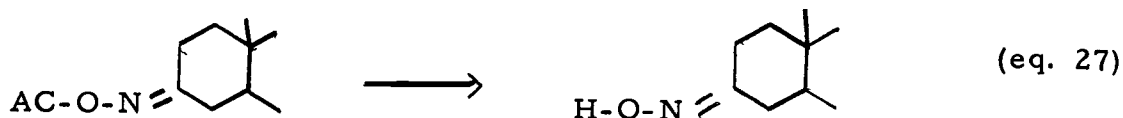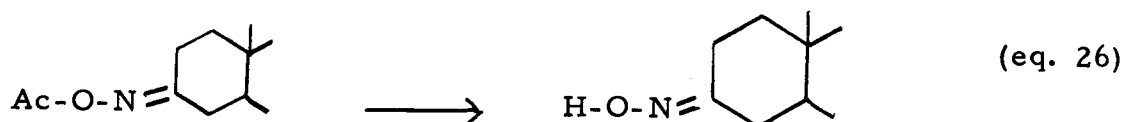Sato reported Z - E isomerization on photolysis of mesityloxide

oxime in ether. He found this to be solvent dependent and gave no

mechanism (40).

The photochemistry of O-alkyl and O-aroyl oximes has been

the topic of several papers. O-alkyl or O-aroyl oximes undergo

photo Z - E isomerization, ketone formation, oxime formation, and

nitrogen-oxygen bond cleavage and recombination of radicals. Pratt,

in 1977, reported O-methyl oximes undergoing photochemical isomerizations (eq. 20) (41). Vermes found ketone formation important as a consequence of irradiation of O-aryl oximes of steroids (eq. 21,22) (42). Photolysis of O-acyl and O-benzoyl oximes gave ketones in yields up to 35% in a study by Beugelmans (eq. 23, 24). He proposed a mechanism using an oxaziridine intermediate (eq. 25) (43).

(eq. 20)

(eq. 21)

(eq. 22)

(eq. 23)

(eq. 24)

$$R_2C=NOR \xrightarrow{h\nu} R_2C=NOR \ S*$$

(eq. 25)

$$R_2C=O + :NR \xleftarrow{h\nu} \left[R_2C \overset{}{\underset{O}{\diagup\!\diagdown}} N-R \right]$$

Oximes were reported by Vermes as major products on irradiation of O-acyl oximes of steroids (eq. 26, 27) (42). In Beugelmans'

study O-acyl oximes were observed to undergo photofragmentation to oximes in yields up to 15% (eq. 28). A mechanism involving homolytic cleavage of the O-C bond was proposed (eq. 29) (43).

$$Ac-O-N= \quad \longrightarrow \quad H-O-N= \qquad \text{(eq. 26)}$$

$$AC-O-N= \quad \longrightarrow \quad H-O-N= \qquad \text{(eq. 27)}$$

$$\begin{array}{c} \phi-C-R \\ \parallel \\ N-OAc \end{array} \quad \longrightarrow \quad \begin{array}{c} \phi-C-R \\ \parallel \\ N-OH \end{array} \qquad \text{(eq. 28)}$$

$$R_2C=N-O-R \quad \longrightarrow \quad R_2C=N-O \cdot + \cdot R \qquad \text{(eq. 29)}$$
$$\downarrow \text{ H abstraction}$$
$$R_2C=NOH$$

Homolytic cleavage of the N-O bond in O-alkyl or O-acyl oximes and recombination of the radicals is another important photodecomposition pathway. Vermes reported this in photodecomposition of O-acyl oximes of steroids (eq. 30) (42). Sato found this to be very important when O-methyl cyclohexanone oxime was irradiated (eq. 31). The mechanism invoked involved homolytic cleavage of the N-O bond and recombination of the radicals (eq. 32) (40). Ishikawa found photodecomposition of O-alkyl or aryl oximes to involve homolytic cleavage of the nitrogen-oxygen bond and recombination of the radicals to form a wide variety of products. The mechanism proposed also involved

the addition of these radicals to the solvent (Scheme VII) (44).

(eq. 30)

(eq. 31)

(eq. 32)
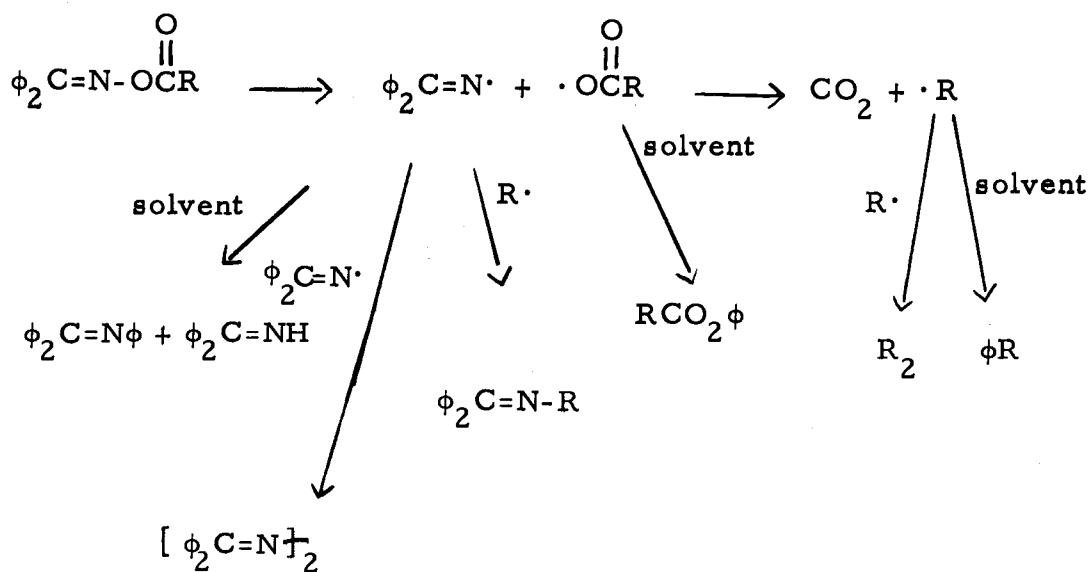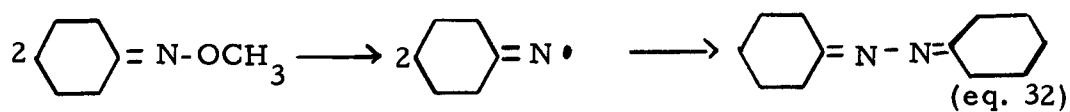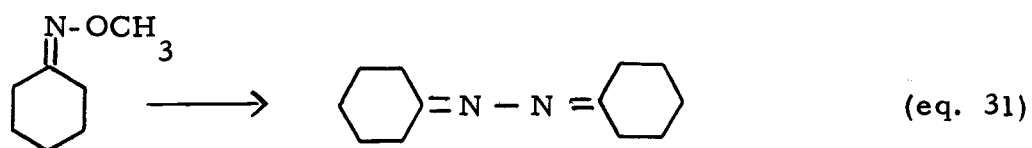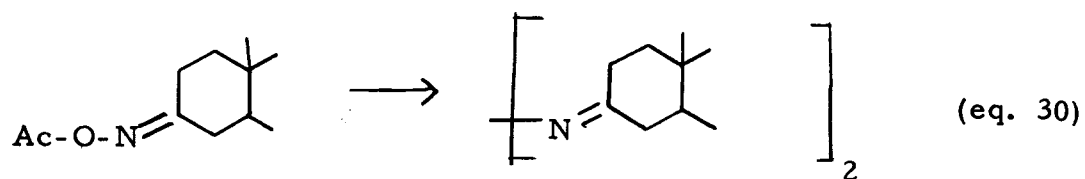
Scheme VII

No photochemistry has been reported to date for aldicarb or any other O-carbamoyl oximes. Ivie and Casida tested aldicarb as a photosensitizer for dieldrin, DDT, diazinon, malathion, sumithion, and carbaryl. They found it to have a slight sensitizing effect for sumithion. They did not report if the aldicarb decomposed (2).
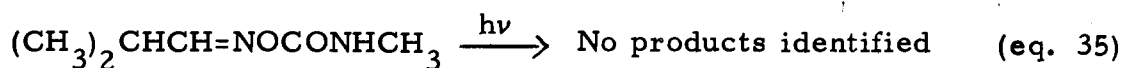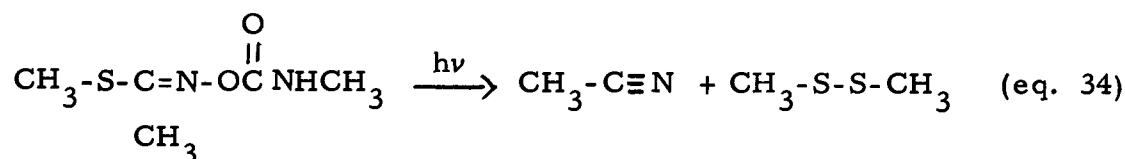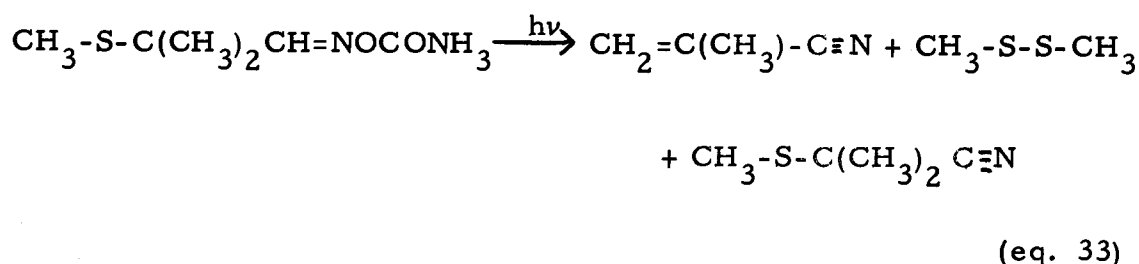
RESULTS AND DISCUSSION

Aldicarb and related compounds are released into the environment as pesticides. Here, they may undergo photoinduced reactions through solar irradiation. Experiments under natural conditions to determine the outcome of these reactions are very cumbersome and difficult to standardize or repeat with reproducible results. The present study is an attempt to mimic the environment in the laboratory with the goal of providing the scientific background necessary to understand the environmental photochemistry of the aldicarb family.

The first irradiations of aldicarb and methomyl were carried out in dilute aqueous solutions (eq. 33, 34). Due to the formation of eight products in addition to those specified in eq. 33 the reaction was simplified by synthesizing and irradiating a model system (eq. 35). Irradiation in water produced several other problems. Since gas chromatography was necessary for analysis, removal of the products from water was required. This was accomplished by continuous ether extraction for 72 hours. Several problems arose from this extraction. First, heating the ether liberated highly volatile components, such as methylamine, from the solution. Secondly, the continuous heating caused thermal decomposition of the photoproducts and starting material. Thirdly, highly water soluble components remained in the water layer. And lastly, quantitative analysis, such as quantum yields, were difficult to obtain. The ether extraction
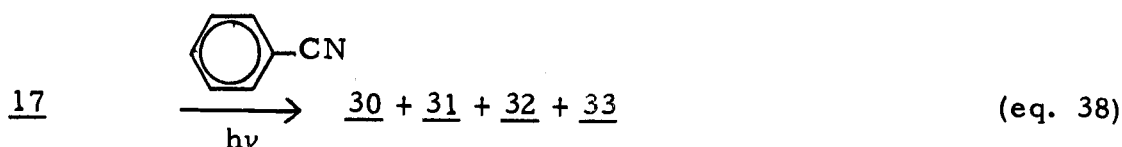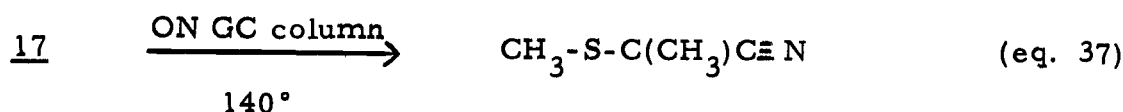
step was hard to standardize since extraction, thermal decomposition,

or volitization varied from one sample to another. To alleviate these

problems the photolyses were carried out in acetonitrile where direct

analysis of the irradiated solution was possible.

$$CH_3-S-C(CH_3)_2 CH=NOCONH_3 \xrightarrow{h\nu} CH_2=C(CH_3)-C\equiv N + CH_3-S-S-CH_3$$

$$+ CH_3-S-C(CH_3)_2 C\equiv N$$

(eq. 33)

$$CH_3-S-\underset{\underset{CH_3}{|}}{C}=N-O\overset{\overset{O}{\|}}{C} NHCH_3 \xrightarrow{h\nu} CH_3-C\equiv N + CH_3-S-S-CH_3$$ (eq. 34)

$$(CH_3)_2 CHCH=NOCONHCH_3 \xrightarrow{h\nu} \text{No products identified}$$ (eq. 35)

Concentrated solutions of aldicarb (0.2 M) (eq. 36) were irradi-

ated in acetonitrile solutions. Photolysis of aldicarb for periods

ranging from one to six hours showed that the major products (30,

31, 32, 33) are results of primary photochemical reactions. By gas

chromatographic analysis the peaks corresponding to starting material

(34, 35) decreased. The nitrile 34 and oxime 35 were thought to be

photoproducts at first. Further experimentation showed them to be

formed thermally on the gas chromatography column. Standard

solutions of aldicarb were injected on the gas chromatograph and

about 46% of the aldicarb formed the nitrile 34 at 140° (eq. 37). The

amount of unreacted aldicarb in an irradiated solution was determined

by ultraviolet spectrometry. In none of the six samples tested was

the amount of nitrile (34) as determined by gas chromatograph more

than 46%. The nitrile observed was a thermal decomposition product.

Reactions sensitized with benzonitrile with light greater than 270 nm

gave the same products as the unsensitized reaction at 2537 Å (eq. 38).

$$CH_3\text{-}S \ C(CH_3)_2CH=NOCONHCH_3 \xrightarrow{h\nu} CH_3NH_2 + CH_3\text{-}S\text{-}S\text{-}CH_3$$

<div align="center">17   30   31</div>

$$+ \quad \underset{32}{N\equiv C\text{-}\overset{\overset{\displaystyle CH_3\text{-}S\text{-}CH_2}{|}}{C}(CH_3)C(CH_3)_2 C\equiv N} + \underset{33}{N\equiv C\text{-}C(CH_3)_2 C(CH_3)_2 C\equiv N}$$

$$+ \underset{34}{CH_3\text{-}S\text{-}C(CH_3)_2\text{-}C\equiv N} + \underset{35}{CH_3\text{-}S\text{-}C(CH_3)_2 CH=NOH}$$

$$+ CH_3NHCONHCH_3 \hspace{4cm} (eq. \ 36)$$

$$\underset{\text{}}{17} \quad \xrightarrow[140°]{\text{ON GC column}} \quad CH_3\text{-}S\text{-}C(CH_3)C\equiv N \hspace{2cm} (eq. \ 37)$$

$$\underset{\text{}}{17} \quad \xrightarrow[h\nu]{\bigcirc\text{-}CN} \quad \underline{30} + \underline{31} + \underline{32} + \underline{33} \hspace{2cm} (eq. \ 38)$$
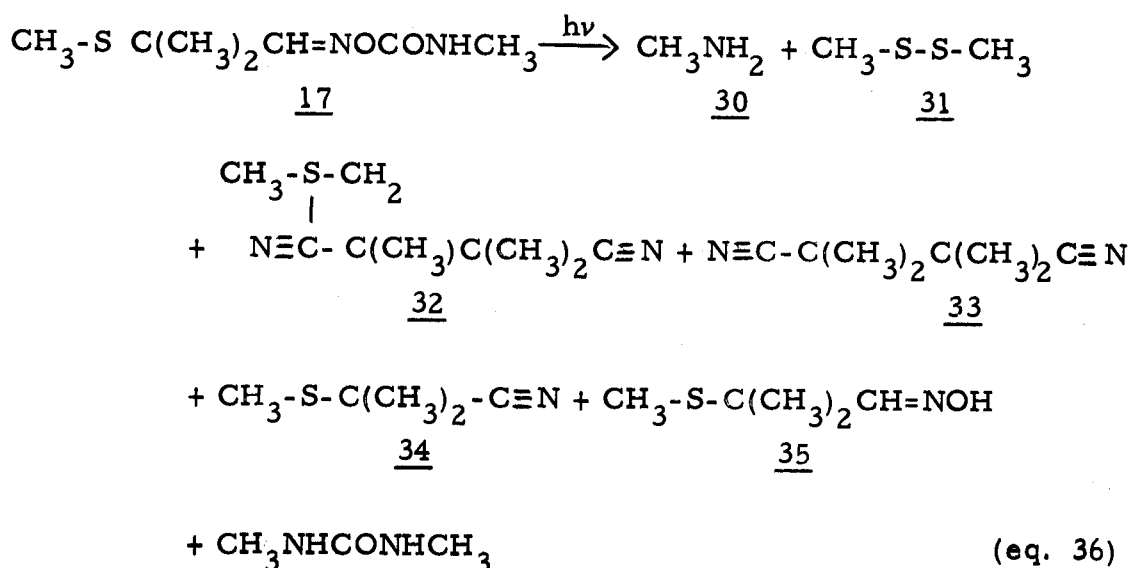
To simplify the reactions and make analysis easier, two model

compounds were synthesized and irradiated. O-(methylcarbamoyl)

isobutyraldehyde oxime 36 and O-(methylcarbamoyl)-trimethyl-

acetaldehyde oxime 37 showed no photochemical reaction after

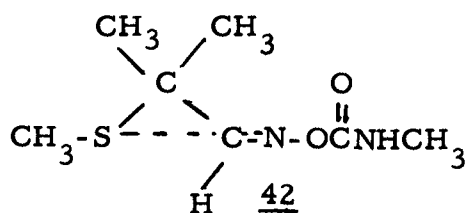irradiation for periods of up to 15 hours. Substrate 36 showed minor photochemical reaction after 15 hours and 37 after 24 hours but no products were identified. The ultraviolet spectra of these compounds (ill. 1) aid in explaining this lack of reactivity. Sulfides normally have λ_{max} less than 230 nm. and ε less than 400 (53). The sulfur containing compounds 17 and 38 have enhanced λ_{max} and ε values which can be attributed to a photodesmotic effect. This effect has been reported before in cyclic unsaturated ketones (54) and cyclic γ keto-sulfides (55, 56). For example, 1-thiacyclooctan-5-one 39 has a λ_{max} of 227 nm. and ε of 2884. Cyclooctanone 40 has no λ_{max} over 200 nm. This is explained by transannular interaction between the sulfur and carbonyl (41) in the excited state. A similar interaction between the sulfur and the imine double bond (42) might very well enhance the λ_{max} and ε values in 17 and 38. This may be the portion of the molecule absorbing light upon irradiation.

$$CH_3\!\!\diagdown\!\!\diagup CHCH=NOCONHCH_3 \qquad CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=NO\overset{O}{\overset{\|}{C}}NHCH_3 \qquad CH_3-S-\underset{CH_3}{\overset{CH_3}{C}}-CH=NOH$$

$$\underline{36} \qquad\qquad\qquad \underline{37} \qquad\qquad\qquad \underline{38}$$

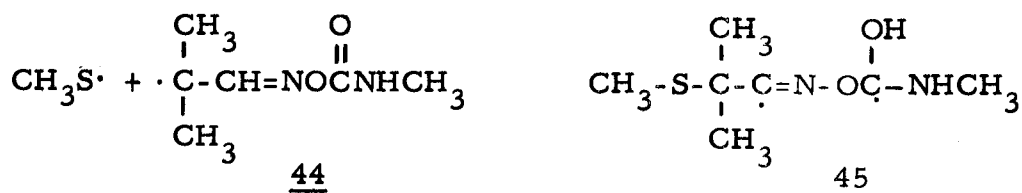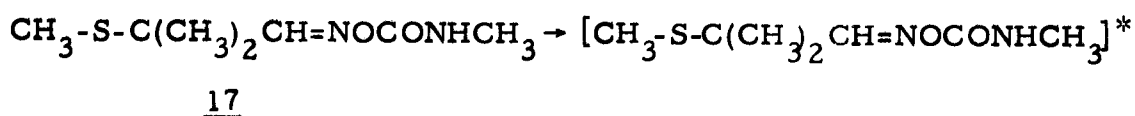$$\underline{39} \qquad\qquad \underline{40} \qquad\qquad \underline{41}$$
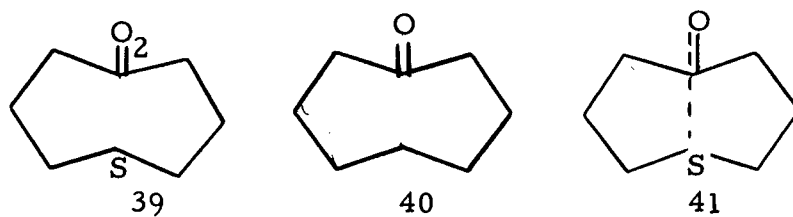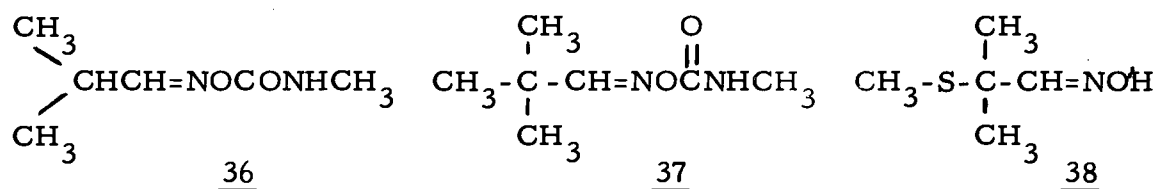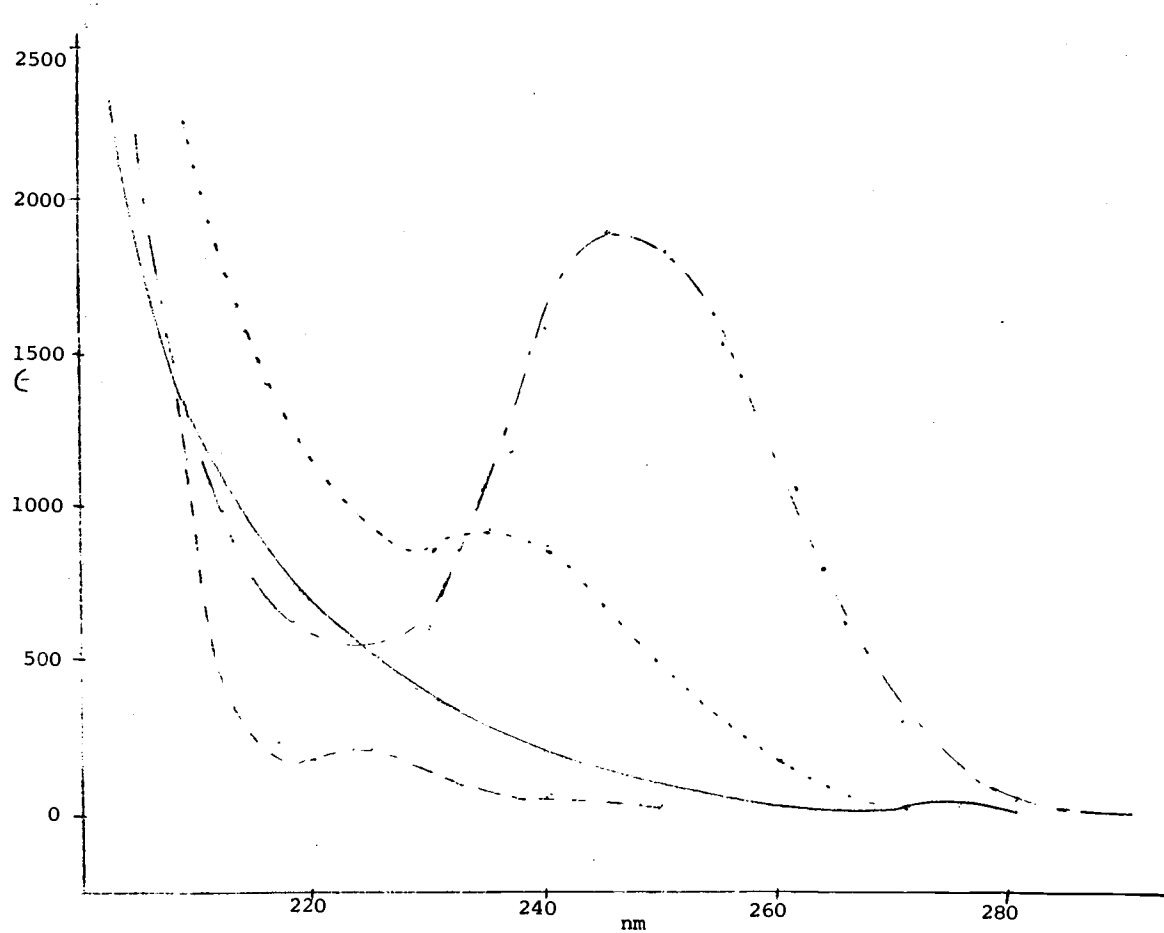
Ill. 1. Ultraviolet Spectra in Acetonitrile: - - - 2-methyl-2-methylthio-O-(methylcarbamoyl) propanal oxime, — — O-(methylcarbamoyl) isobutyraldehyde oxime, — O-(methylcarbamoyl) trimethylacetaldehyde oxime, · · · 2-methyl-2-methylthiopropanal oxime. Trimethylacetaldehyde ocime and isobutyraldehyde oxime showed no λ_{max} above 200 nm.

$$CH_3\text{-}S \cdots \overset{\overset{\displaystyle CH_3 \diagup CH_3}{\diagdown C \diagup}}{\underset{H}{\overset{\diagdown}{C}}}\text{-}N\text{-}O\overset{O}{\overset{\|}{C}}NHCH_3$$
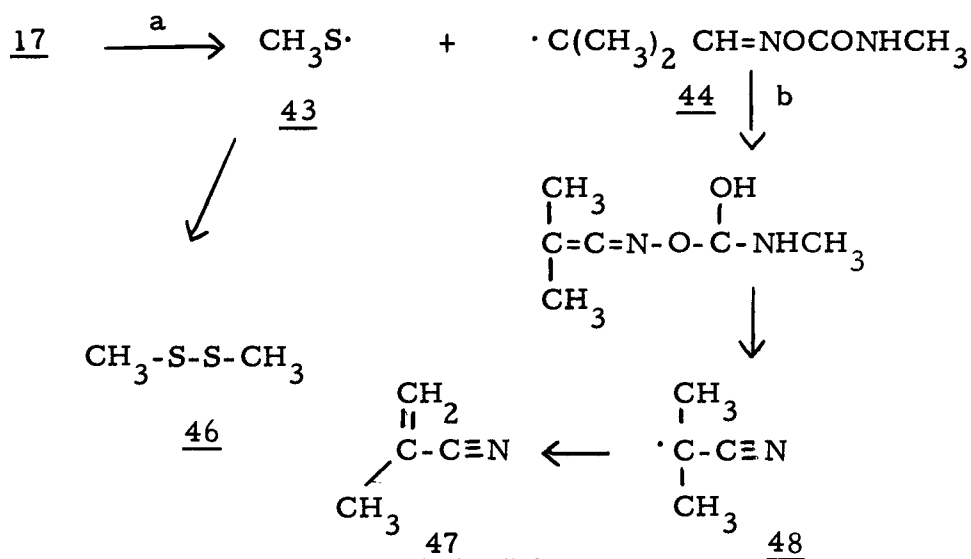
$$\underline{42}$$

Mechanisms involving two major decomposition pathways could explain the products observed on irradiation of aldicarb. Comparison of the triplet sensitized and unsensitized reactions indicates that they both proceed through the triplet state. These possible routes of decomposition are homolytic cleavage of the sulfur-carbon bond (a) to form radicals 43 and 44 or abstraction of the imine hydrogen by the carbonyl oxygen through a six membered transition state to form the diradical 45 (Scheme VIII). Further reactions depend on the conditions.

$$CH_3\text{-}S\text{-}C(CH_3)_2CH\text{=}NOCONHCH_3 \rightarrow [CH_3\text{-}S\text{-}C(CH_3)_2CH\text{=}NOCONHCH_3]^*$$

$$\underline{17}$$

$$CH_3S\cdot \; + \; \cdot\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}CH\text{=}NO\overset{O}{\overset{\|}{C}}NHCH_3 \qquad\qquad CH_3\text{-}S\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}\overset{\cdot}{C}\text{=}N\text{-}O\overset{OH}{\overset{|}{C}}\text{-}NHCH_3$$

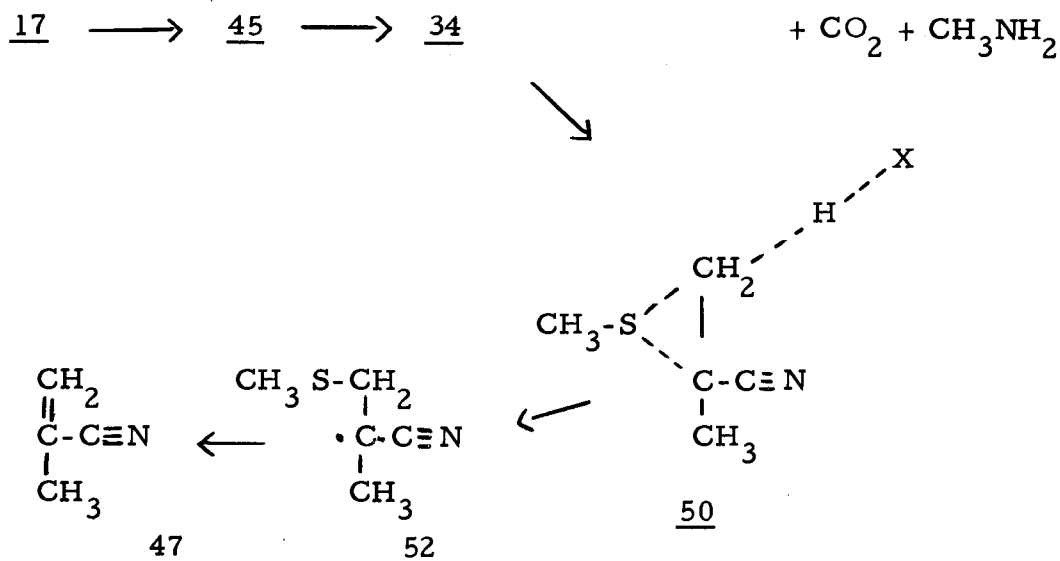$$\underline{44} \qquad\qquad\qquad\qquad\qquad \underline{45}$$

Scheme VIII

Irradiation of dilute aqueous solutions of aldicarb results in two major products (46) and 47). Radical 43 dimerizes to form

dimethyldisulfide ($\underline{46}$). Also, α methylacrylonitrile ($\underline{47}$) could form via

two possible mechanisms. Path (a) could lead to radical $\underline{44}$ which

could undergo intramolecular hydrogen abstraction followed by nitro-

gen-oxygen bond cleavage to give radical $\underline{48}$. This could lose a

hydrogen atom to produce 47 (Scheme IX). Another possible mechan-

ism is hydrogen abstraction (b) followed by nitrogen-oxygen bond

cleavage to give the nitrile $\underline{34}$. Bridging by the methylthio group (50)

could give anchimeric assistance to the hydrogen abstraction generat-

ing $\underline{52}$, which might lose a methylthio radical to form α methyl-

acrylonitrile (Scheme X). The second seems more likely since the

hydrogen abstraction step is assisted. The first mechanism requires

that radical $\underline{44}$ exists long enough to allow elimination to take place.

This seems unlikely since the radical can not be delocalized onto the

nitrogen during this step. The second mechanism will be discussed

in more detail later.

$$\underline{17} \xrightarrow{\quad a \quad} CH_3S\cdot \quad + \quad \cdot C(CH_3)_2\,CH=NOCONHCH_3$$

$$\underline{43} \qquad\qquad \underline{44} \Big| b$$

$$\begin{array}{cc} CH_3 & OH \\ | & | \\ C=C=N-O-C-NHCH_3 \\ | \\ CH_3 \end{array}$$

$$CH_3-S-S-CH_3$$

$$\underline{46}$$

$$\begin{array}{c} CH_2 \\ \| \\ C-C\equiv N \\ / \\ CH_3 \end{array} \longleftarrow \begin{array}{c} CH_3 \\ | \\ \cdot C-C\equiv N \\ | \\ CH_3 \end{array}$$

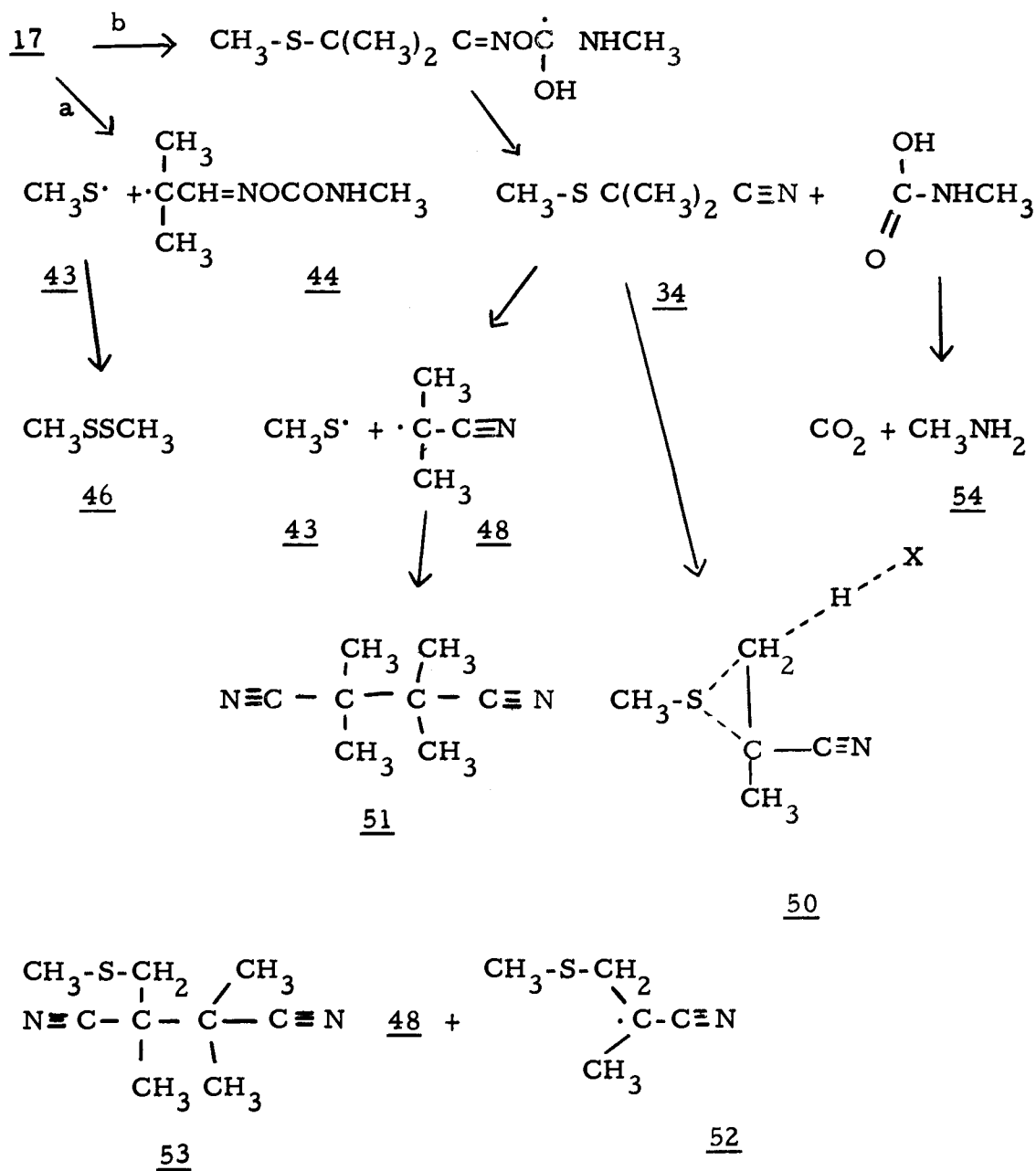$$\underline{47} \qquad\qquad \underline{48}$$

Scheme IX

Scheme X

If the irradiation conditions are changed to a more concentrated solution in acetonitrile the same two major decomposition pathways can take place, but several different products are formed. As in the dilute aqueous solutions the sulfur bond cleaves to form radicals 43 and 44. Radical 43 then dimerizes to form dimethyldisulfide (46). Hydrogen abstraction by the carbonyl oxygen followed by nitrogen oxygen bond cleavage to form the nitrile 34 also takes place. This cleaves homolytically to form radical 48 and 43. The radical 48 then dimerizes to form tetramethylsuccinonitrile 51. Nitrile 34 may also undergo hydrogen abstraction through a bridged sulfide 50 to produce radical 52. This radical can add to 48 to produce 1-(methyl-thio)-2,3-dicyano-2,3-dimethylbutane (53) (Scheme XI).
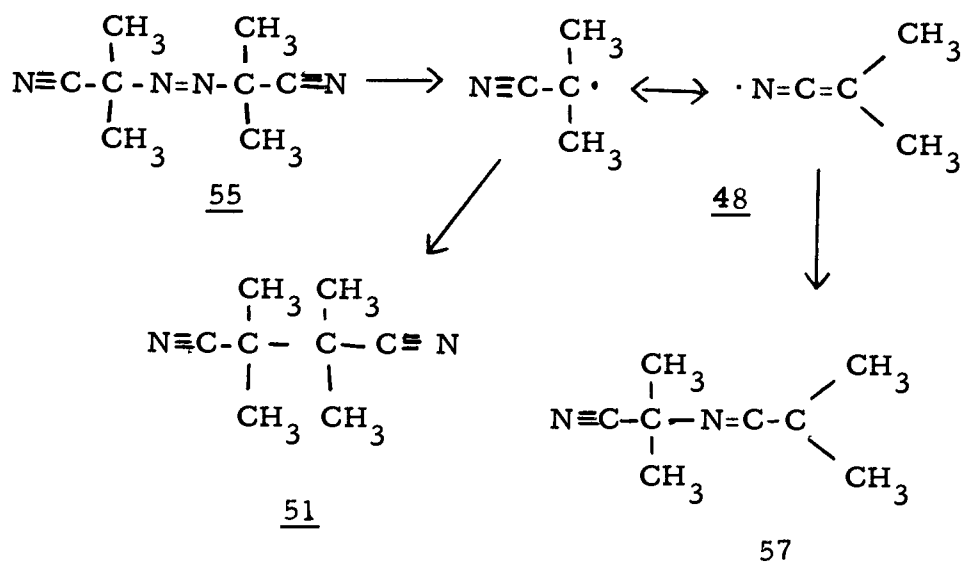
$17 \xrightarrow{b} CH_3-S-C(CH_3)_2 \overset{\cdot}{C}=NO\overset{\cdot}{C}\ NHCH_3$
                                                        $\underset{OH}{|}$

$17 \xrightarrow{a}$

$CH_3S\cdot + \cdot\underset{CH_3}{\overset{CH_3}{|}}CCH=NOCONHCH_3$
43   **44**

$CH_3-S\ C(CH_3)_2\ C\equiv N +$ **34**
$\underset{O}{\overset{OH}{\underset{\|}{C}}}-NHCH_3$

CH_3SSCH_3
46

$CH_3S\cdot + \cdot\underset{CH_3}{\overset{CH_3}{|}}C-C\equiv N$
43   **48**

$CO_2 + CH_3NH_2$
54

$N\equiv C - \underset{CH_3}{\overset{CH_3}{|}}C - \underset{CH_3}{\overset{CH_3}{|}}C - C\equiv N$
51

$CH_3-S\overset{CH_2\cdots H\cdots X}{\diagup}$
$\qquad\diagdown\underset{CH_3}{\overset{|}{C}}-C\equiv N$
50

$\underset{CH_3}{\overset{CH_3-S-CH_2}{}}$
$N\equiv C-\underset{CH_3}{\overset{|}{C}}-\underset{CH_3}{C}-C\equiv N$ **48** +
53

CH_3-S-CH_2
$\cdot C-C\equiv N$
$\underset{CH_3}{}$
52

Scheme XI

These recombination routes have precedence in the photo-decomposition of azobisisobutyronitrile (AIBN) (**55**) to radical **48** (57). This radical is relatively stable due to delocalization onto the nitrogen (**48**). Because of its stability radical **48** exists long enough to react
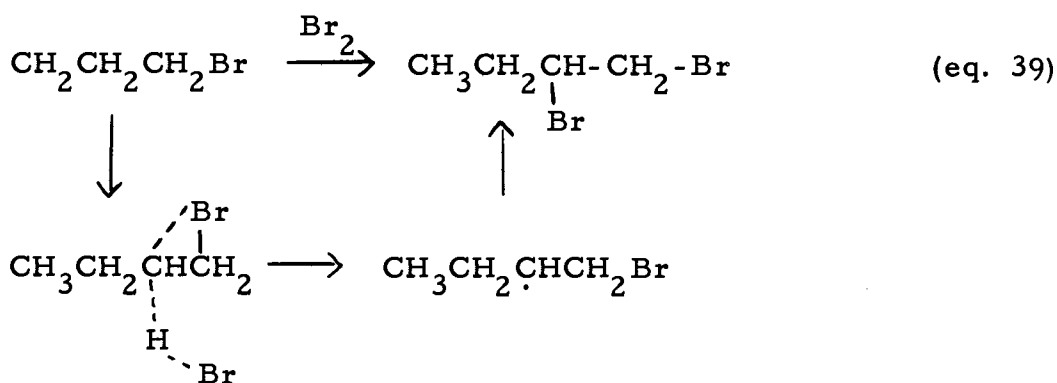
with some other radical. It dimerizes to form the symmetrical

product 51 and an unsymmetrical ketenimine 57. Tetramethyl-

succinonitrile (51) is the predominant product (57). This is analogous

to reactions in the photodecomposition of aldicarb. The "symmetrical"

products are the only ones observed and delocalization of radicals 48

and 52 allows them to exist long enough to couple with another radical.

$$N \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - N = N - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - C \equiv N \longrightarrow N \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} \cdot \longleftrightarrow \cdot N = C = C \overset{CH_3}{\underset{CH_3}{\diagdown}}$$

$$\underset{55}{} \qquad\qquad \underset{48}{}$$

$$N \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - C \equiv N$$

$$\underset{51}{}$$

$$N \equiv C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - N = C - C \overset{CH_3}{\underset{CH_3}{\diagdown}}$$
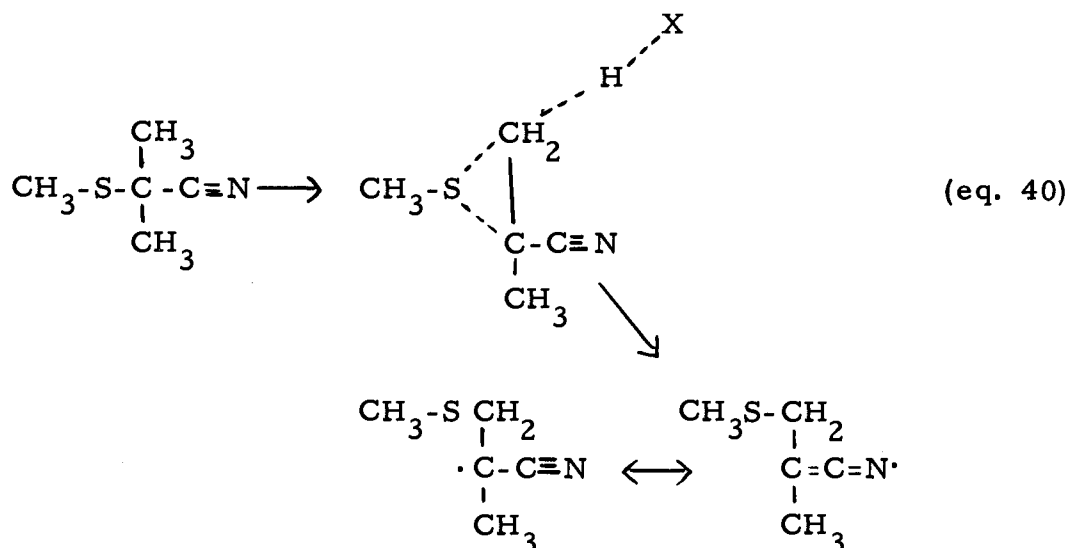
$$\underset{57}{}$$

The bridged sulfide intermediate 50 has precedence in the

bromination of 1-bromobutanes. The predominant dibromo product

on free radical bromination of 1-bromobutanes is the 1,2 disubstituted

compound (eq. 39). Normally, electronegative substituents decrease

the amount of 1,2 disubstitution in free radical reactions. This

anomaly is explained by a bridging bromine giving anchimeric assis-

tance to hydrogen abstraction (scheme XII). A requirement for this

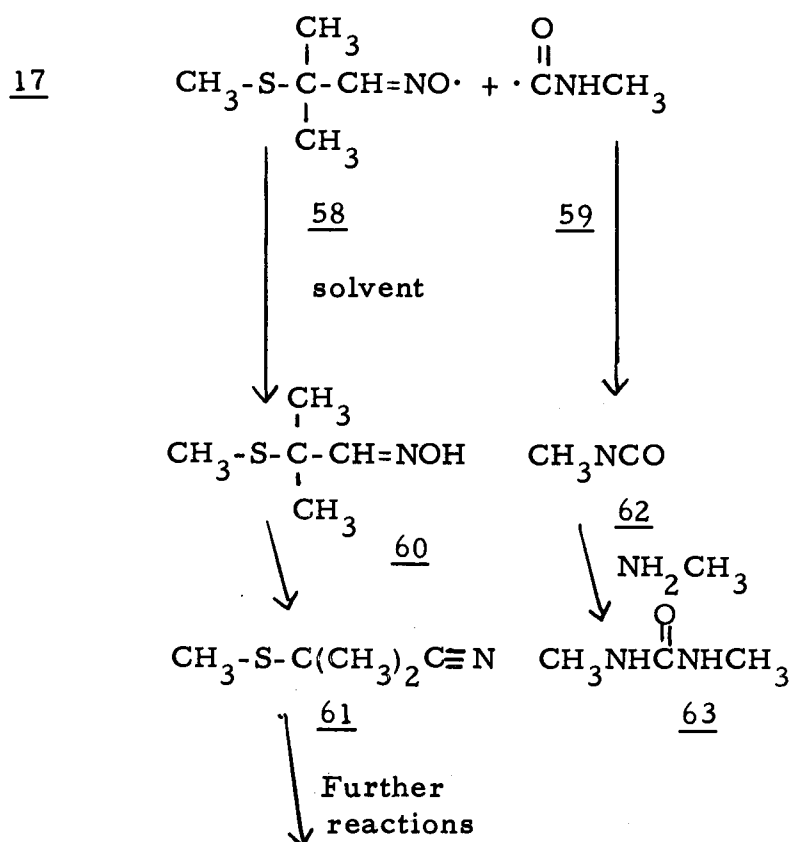is an antiperiplanar arrangement of the bromine to the abstracted

hydrogen. Generally, the product formed is the most stable radical (58). Also, in several cases sulfides have been found to form bridged radical intermediates (59). This supports the bridged sulfide <u>50</u> mechanism invoked above. The sulfur and abstracted hydrogen can take an antiperiplanar configuration. The resultant radical from the 1,2 methylthio shift is α to the nitrile and therefore a more stable radical. The radical <u>50</u> can then react with radical <u>48</u> to form <u>53</u> (eq. 40).

$$CH_2CH_2CH_2Br \xrightarrow{Br_2} CH_3CH_2CH-CH_2-Br \qquad (eq.\ 39)$$

$$\downarrow \qquad\qquad \uparrow Br$$

$$CH_3CH_2\overset{Br}{\underset{H}{\overset{|}{C}}HCH_2}\ \overset{Br}{} \longrightarrow CH_3CH_2\underset{\cdot}{C}HCH_2Br$$

<center>Scheme XII</center>

$$CH_3-S-\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}-C\equiv N \longrightarrow CH_3-S\overset{\displaystyle CH_2}{\underset{\displaystyle \overset{|}{C}-C\equiv N}{\big|}} \qquad (eq.\ 40)$$

$$CH_3-S\ \underset{\overset{|}{CH_3}}{\overset{CH_2}{\cdot C-C\equiv N}} \longleftrightarrow CH_3S-\underset{\overset{|}{CH_3}}{\overset{CH_2}{C=C=N\cdot}}$$

Another minor route is involved in the photodecomposition of

aldicarb. Homolytic cleavage of the oxygen-carbon bond produces

radicals 58 and 59. Radical 58 can abstract an hydrogen to form

the oxime 60 and isocyanate (62). The oxime 60 was not isolated,

and may react further to form the nitrile 61. Isocyanate (62) can

react with methylamine to produce 1,3-dimethylurea (63) (Scheme XII).

17   CH_3-S-$\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}$-CH=NO· + ·$\overset{\overset{O}{||}}{C}$NHCH$_3$

58   59

solvent

CH_3-S-$\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}$-CH=NOH   CH$_3$NCO

60   62

NH$_2$CH$_3$

CH_3-S-C(CH_3)$_2$C≡N   CH$_3$NH$\overset{\overset{O}{||}}{C}$NHCH$_3$

61   63

Further
reactions

Scheme XIII

Quantum yield data adds further information on the mechanisms

involved in the photodecomposition of aldicarb. Data was collected

on the four major products in acetonitrile (Table 1). Methylamine and

Table 1. Quantum Yield Data

Compound	Quantum yield	Standard deviation	Percent yield
	Unsensitized Reaction (average of 4 runs)		
CH_3NH_2 54	0.93	0.13	54
CH_3SSCH_3 46	0.55	0.027	63
$N{\equiv}C\text{-}C\text{-}C\text{-}C{\equiv}N$ (with CH_3, CH_3, CH_3, CH_3) 51	0.062	0.0064	7.2
$N{\equiv}C\text{-}C\text{-}C\text{-}C{\equiv}N$ (with CH_3, CH_2SCH_3, CH_3, CH_3) 53	0.024	0.0052	4.4
	Sensitized Reaction (average of 2 runs)		
CH_3NH_2 54	0.89		53
CH_3SSCH_3 46	0.12		15
$N{\equiv}C\text{-}C\text{-}C\text{-}C{\equiv}N$ (with CH_3, CH_3, CH_3, CH_3) 51	...*		...*
$N{\equiv}C\text{-}C\text{-}C\text{-}C{\equiv}N$ (with CH_3, CH_2SCH_3, CH_3, CH_3) 53	0.017		2.1

*Sensitizer hindered analysis of this component.

dimethyldisulfide form with much greater efficiency than tetramethyl-succinonitrile and 1-(methylthio)-2, 3-dicyano-2, 3-dimethylbutane. The cleavage of the sulfur-carbon bond (path a) and the carbonyl oxygen hydrogen abstraction (path b) take place to a much greater extent than the recombinant routes. The remainder of the unrecovered molecule must dimerize to nonvolatile components which were un-detectable under the gas chromatographic conditions used in analysis.

The information gathered about the photolysis of aldicarb has some environmental implications. Aldicarb undergoes photodecomposition in the presence of a sensitizer in light greater than 270 nm. This is approximately the wavelength region available at the earth's surface. So, photoexcitation and degradation of aldicarb in the presence of any naturally available sensitizers is possible in the environment.

EXPERIMENTAL

Melting points were obtained on a Buchi melting point apparatus and are uncorrected. A Varian HA-100 was used to record the NMR spectra at 100 MHz. Infrared spectra were obtained with a Perkin-Elmer 727B infrared spectrophotometer. A Cary 15 spectrophotometer was used to record the ultraviolet spectra. Mass spectra were recorded on an Atlas CH7 mass spectrophotometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. VPC analyses were carried out on a F and M Model 700 chromatograph equipped with dual columns and thermal conductivity detectors or a programmable Varian Aerograph Series 1200 chromatograph equipped with a flame ionization detector. The following columns were used: A) 20' x 1/8" O.D. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60/80; B) 4' x 1/4" O.D. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60/80; C) 10' x 1/8" O.D. 8% OV 101 aluminum column on Chromosorb Q, 100/120; D) 4' x 1/8" O.D. 5% Carbowax 20M and 10% DC 200 on Chromosorb G NAW, 60/80; E) 10' x 1/8" O.D. 5% Carbowax 20M and 10% DC 200 aluminum column on Chromosorb G NAW, 60/80; F) 10' x 1/4" O.D. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60/80; and G) 12' x 1/4" O.D. 5% OV 17 aluminum column on Chromosorb Q, 100/120. Product quantities for quantum yields were calculated from chromatographic data based on relative peak areas measured by Hewlett-Packard

3373B Integrator. Photolyses were carried out with a Rayonet 2537 Å mercury lamp or a Hanovia 450 watt high pressure mercury lamp fitted with several filters. Quantum yields were run in a merry-go-round apparatus using either lamp.

Preparation of Butyraldehyde Oxime

Hydroxylamine hydrochloride (10.6 g, 0.15 mol) was dissolved in 100 ml of water in a 250 ml erlenmeyer flask. Butyraldehyde (8.2 g, 0.11 mol) was added from an addition funnel. The mixture was warmed to 45-50° for a few min and then cooled in the refrigerator for about 2 hr. The organic layer was separated from the aqueous layer and distilled. The residue was distilled to provide 8.8 g of the product (92%); NMR ($CDCl_3$, 100 MHz) δ 10.3 (1 H), 7.3 and 6.6 (1 H), 2.3 to 1.7 (2 H), 1.6 to 1.1 (2 H), 1.1 (3 H).

Preparation of Acetone Oxime

An adaptation of the method of Vogel (45) was employed. A solution of hydroxylamine hydrochloride (6.5 g, 0.094 mol) and sodium hydroxide (3.3 g, 0.083 mol) in 20 ml of water was prepared and cooled in an ice bath. Acetone (6.0 g, 0.10 mol) was added slowly. The flask was stirred and placed in a refrigerator to cool. The crystalline product was filtered off to yield 6.7 g of the oxime (92%) with mp 45°. The mass spectrum gave $\underline{m/e}$ 73.

Preparation of Isobutyraldehyde Oxime

Hydroxylamine hydrochloride (25.0 g, 0.36 mol) and sodium hydroxide (5.5 g, 0.14 mol) were dissolved in 100 ml water. Isobutyraldehyde (40.9 g, 0.57 mol) was dripped in slowly and the mixture was stirred at 50-60° for 3 hr. The organic layer was separated and distilled at aspirator pressure to yield 10.0 g of the oxime (20.5%); NMR (CDCl$_3$, 100 MHz) δ 8.3 (1 H), 7.3 and 6.5 (1 H), 3.2 and 2.5 (1 H), 1.1 (6 H); ir (neat) ν 3350 (O-H stretching), 1640 (C=N stretching) cm^{-1}.

Preparation of Trimethylacetaldehyde Oxime

A solution of hydroxylamine hydrochloride (7.0 g, 1.0 mol) and sodium hydroxide (2.0 g, 0.05 mol) in 100 ml of water was prepared. The aldehyde (7.9 g, 0.092 mol) was dripped in slowly and the mixture was stirred 2 hr at 65°. After the mixture was cooled overnight a crystalline product was filtered with a Buchner funnel to produce 5.48 g of the oxime (59%); NMR (CDCl$_3$, 100 MHz) δ 9.0 (1 H), 7.4 (1 H), 1.1 (9 H); ir (film) ν 3300 (O-H stretching), 1640 (C=N stretching) cm^{-1}; mass spectrum $\underline{m/e}$ 101.

Hydrolysis of Methyl Methacrylate to Methacrylic Acid

A solution of methyl methacrylate (10.0 g, 0.10 mol) and sodium hydroxide (6.0 g, 9.15 mol) in 50 ml of water was heated at reflux for

2 hr. The methanol formed was distilled off and the solution was acidified with dilute hydrochloride acid. It was extracted with 3 x 25 ml of ether, which was removed by distillation at aspirator pressure to give 1.5 g of the acid (17%); NMR (CDCl$_3$, 100 MHz) δ 10.2 (1 H), 5.8 (1 H), 5.3 (1 H), 1.6 (3 H); mass spectrum $\underline{m/e}$ 86.

Hydrolysis of O-(methylcarbamoyl)-2-methyl-2-methylthiopropanal oxime (17) to 2-methyl-2-methylthiopropanal oxime (35)

The method of Payne (5) was adapted for use in this laboratory. Sodium hydroxide (1.0 g, 0.025 mol) and O-(methylcarbamoyl)-2-methyl-2-methylthiopropanal oxime (3.2 g, 0.017 mol) were dissolved in 12.5 ml of methanol and 37.5 ml of water. The solution was stirred for 64 hr, neutralized to pH 7 with dilute hydrochloric acid, and extracted with 4 x 10 ml of isopropyl ether. The ether was removed by distillation at aspirator pressure to yield 1.85 g (82%) of the oxime; NMR (CDCl$_3$, 100 MHz) δ 9.1 (1 H), 7.3 (1 H), 2.0 (3 H), 1.4 (6 H); ir (neat) ν 3330 (O-H stretching) cm^{-1}; mass spectrum $\underline{m/e}$ 133.

Preparation of O-(methylcarbamoyl)-isobutyraldehyde oxime (36)

A solution of isobutyraldehyde oxime (7.34 g, 0.084 mol) in 25.0 ml of acetonitrile was prepared in a three necked flask under nitrogen. Triethylamine (0.73 g, 0.0072 mol) and an excess of methylisocyanate were added slowly and the solution was stirred for

20 hr. The solvent and excess methylisocyanate were removed by distillation at room temperature and aspirator pressure. Column chromatography of a 4" x 2" silica gel column with chloroform as eluent was used to purify the syrupy residue. The product was collected and the solvent removed on the roto-evaporator to give 8.0 g (66%) of O-(methylcarbamoyl)-isobutyraldehyde oxime with mp 70-73°; NMR (CDCl$_3$, 100 MHz) δ 7.7 and 7.3 (1 H), 6.6 (1 H), 2.9 to 2.7 (3 H), 2.7 to 2.4 (1 H), 1.2 to 1.0 (6 H); ir (film) v 1730 (C=O stretching), 1660 (C=N stretching) cm^{-1}; mass spectrum $\underline{m/e}$ 144.

Preparation of O-(methylcarbamoyl)-trimethylacetaldehyde oxime (37).

2,2-trimethylacetaldehyde oxime (4.4 g, 0.043 mol) was dissolved in 15 ml of acetonitrile in a 3 necked flask under nitrogen. Methylisocyanate (3.8 g, 0.066 mol) and 5 drops triethylamine were added dropwise. The solution was stirred 21 hr at 0° in an ice bath. Removal of the solvent and excess methylisocyanate at 20° and aspirator pressure left a residue which was refrigerated overnight in a small portion of acetonitrile. The crystalline product was filtered with a Buchner funnel to give 3.9 g (58%) with a mp 76-77°; NMR (CDCl$_3$, 100 MHz) δ 7.6 (1 H), 6.1 (1 H), 2.9 (3 H), 1.2 (9 H); ir (film) v 1730 (C=O stretching), 1640 (C=N stretching) cm^{-1}; mass spectrum $\underline{m/e}$ 158.

Anal. Calcd for $C_7H_{14}N_2O_2$: C, 53.13; H, 8.94. Found: C, 53.05; H, 8.68.

Preparation of Dimethyl-N-(2-cyano-2-propyl)-ketenimine (37)

The method of Smith was used (46). Distillation of the product at 2 torr and 28° produced about 0.2 g (25%); NMR (CDCl$_3$, 100 MHz) δ 1.71 (3 H), 1.55 (3 H); ir (neat) ν 2250 (C N stretching), 2050 (C=C=N stretching) cm^{-1}, mass spectrum: m/e 69 (100), 68 (38), 41 (28), 42 (18), 54 (17), ...94 (3), 121 (4).

Preparation of Tetramethylsuccinonitrile (51)

Again a method of Smith's was used (46). Crystallization of the product gave 0.45 g (68%); NMR (CDCl$_3$, 100 MHz) δ 1.54; ir (film) ν 2250 (C N stretching) cm^{-1}. The mass spectrum is the same as the spectrum of dimethyl-N-(2-cyano-2-propyl)-ketenimine.

Photolysis of Aldicarb (17) in Water

Aldicarb (3.5 g, 0.1ρ mol) was dissolved in 500 ml of water in a large reaction flask. The solution was degassed by bubbling nitrogen through it for 1 hr and irradiated (Hanovia) through quartz for 5 hr. The resultant yellow solution was continuously extracted with 500 ml of ether for 72 hr. The ether layer was concentrated to 25 ml and

analyzed by GC-MS using column A at 100-190°. Of the 11 peaks

observed mass spectra were obtained for 10. Peak 2 was the solvent

diethyl ether. Peaks 3, 4, 7, 9, 10, and 11 were small and were not

identified. By comparison of published mass spectra peaks 5 and 6

were identified as α-methylacrylonitrile (47) (5%) and dimethyl-

disulfide (48) (5%) respectively. NMR and ir spectra were also

obtained on peak 8 by preparative GC and it was identified as 2-methyl-

2-methylthiopropanenitrile; NMR (CDCl$_3$, 100 MHz) δ 2.35 (3 H,

singlet, CH$_3$-S), 1.7 (6 H, singlet, (CH$_3$)$_2$-C); ir (neat) ν 2210 (C N

stretching) cm^{-1}; mass spectrum m/e 115.

Photolysis of O-(methylcarbamoyl)-isobutyraldehyde Oxime (36) in Water

A solution of O-(methylcarbamoyl)-isobutyraldehyde oxime (1.3

g, 0.090 mol) in 100 ml of water was placed in a quartz tube, degassed

as above and irradiated (Hanovia) for 10 hr. This solution was con-

tinuously extracted with ether for 72 hr. The ether layer was concen-

trated and analyzed by GC-MS on column A at 100 to 175°. Minor

photochemical reaction was observed, but no peaks were identified.

Photolysis of Methomyl in Water

Methomyl in water was degassed and irradiated (Hanovia)

through quartz for 3 hr. The extraction was the same as in the previ-

ous photolysis. Analysis by GC-MS on column B at 70° produced 6

peaks. Peak 1 was the solvent diethyl ether. Peak 2 was identified

as acetonitrile by comparison to an authentic sample. Comparison of

peak 3 to a published spectrum (48) proved it to be dimethyldisulfide.

Peaks 4, 5, and 6 were small and were not identified.

Photolysis of Aldicarb in Acetonitrile

Several photolyses were carried out according to the same

procedure. A solution of aldicarb (0.60 g, 0.0031 mol) in 10.0 ml

acetonitrile was placed in a resealable quartz tube and degassed by

5 repeated freeze-thaw cycles at 1×10^{-5} torr. It was irradiated with

2537 Å light (Rayonet) for 6 hr. The photoproducts were analyzed by

GC-MS with two columns. Column A at 90° produced 4 peaks. The

first peak was identified as methylamine by comparison to a published

mass spectrum (49). Peaks 2, 3, and 4 were very small and were

not identified. Fourteen peaks were observed on column D at 60-180°.

Peak 2 was the solvent acetonitrile. Peaks 1, 7, 8, 12, 13, and 14

were small and were not identified. Peaks 3 and 9 were identified

as dimethyl-disulfide (48) and 1,3-dimethyl urea (50) by comparison

to published spectral data. Comparison to authentic samples proved

peaks 6 and 11 to be 2-methyl-2-methylthiopropanal oxime and

α-methylacrylic acid respectively. NMR and ir were also obtained

for peaks 4, 5, and 10 from samples obtained by preparative GC on

column B. Peak 4 was identified as 2-methyl-2-methylthiopropane-nitrile by comparison to the spectra of peak 8 in the photolysis of aldicarb in water. Comparison of the spectra of an authentic sample to peak 5 proved it to be tetramethylsuccinonitrile (mass spectrum ill. 2). Peak 10 was identified as 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane from its spectra; NMR (CDCl$_3$, 100 MHz) δ 2.8 (2 H, -CH$_2$-), 2.3 (3 H, CH$_3$-S), 1.6 (3 H, CH$_3$-C-CH$_2$-S-), 1.5 (6 H, (CH$_3$)$_2$-C-); ir (neat) v 2240 (CN stretching) cm^{-1}; mass spectrum m/e 182 (ill. 3).

## Photolysis of Aldicarb in Acetonitrile over Different Time Periods

A series of photolyses were carried out according to the above procedure for 1, 2, 3, 4, and 6 hr. Analysis on column D at 60 - 180° showed 2-methyl-2-methylthiopropanonitrile and 2-methyl-2-methyl-thiopropanal oxime decreased with time, while methylamine, dimethyl-disulfide, tetramethylsuccinonitrile, and 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane increased with time (ill. 4).

Photolysis of Aldicarb with Sensitizers

Aldicarb was irradiated with three sensitizers using the same general procedure as above. Benzophenone (0.30 M, Hanovia, pyrex) produced the same major products as the unsensitized reaction in low
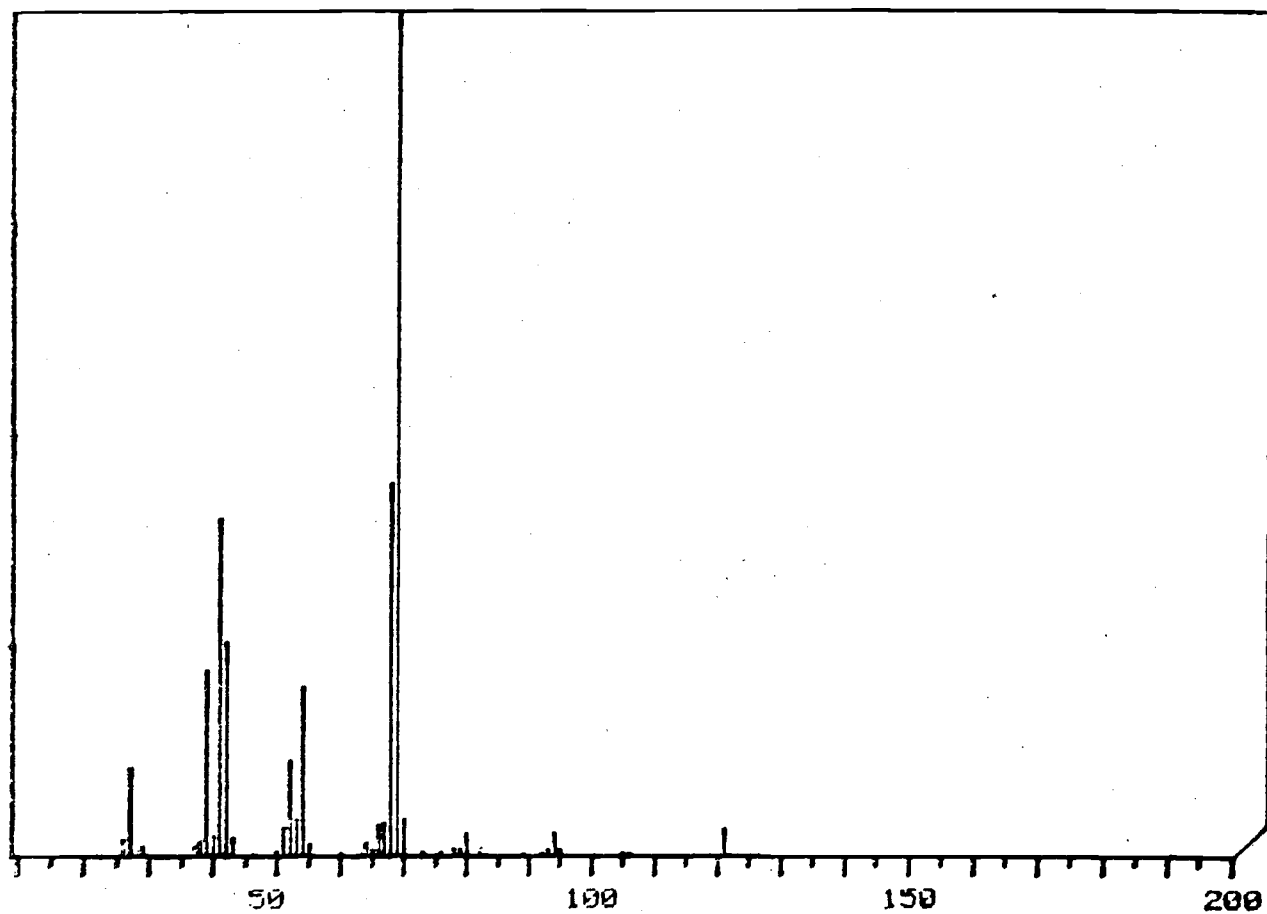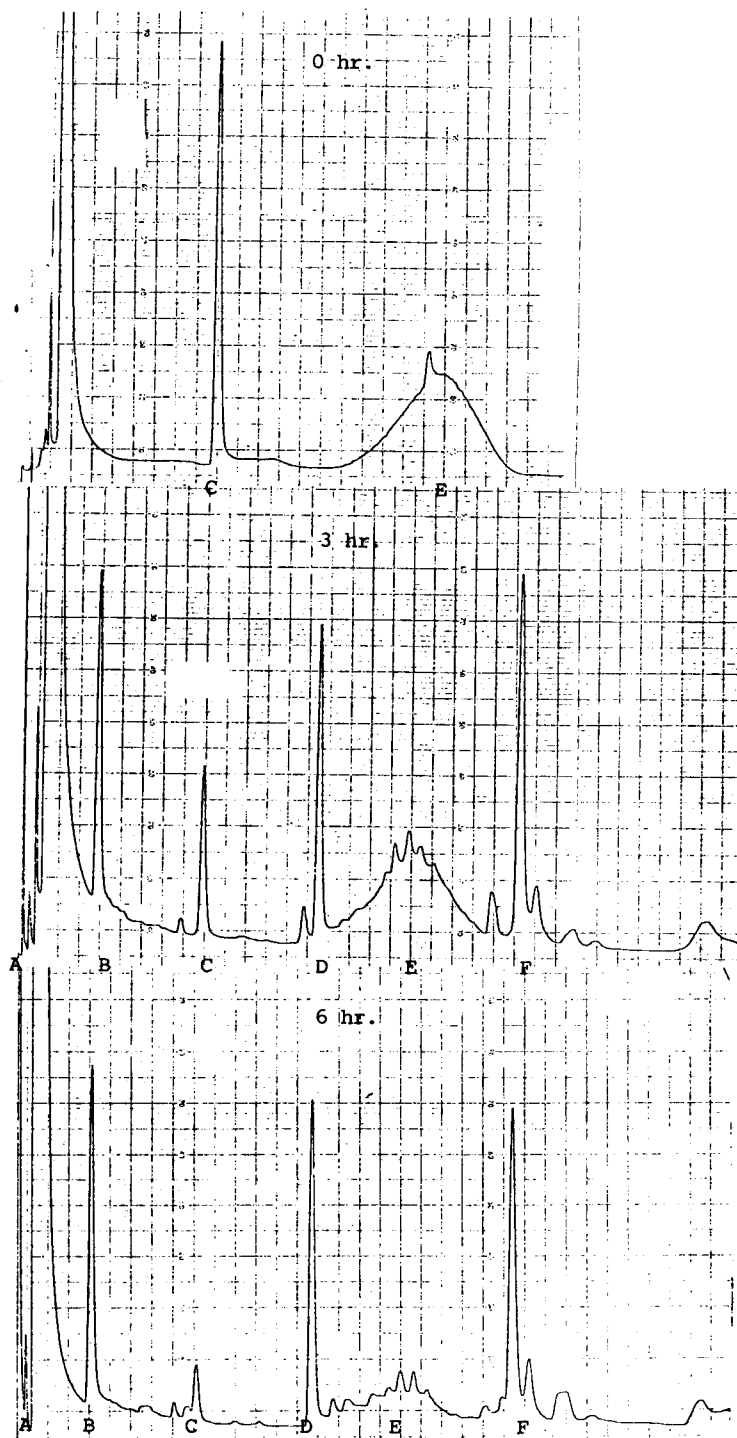
Ill. 2. Mass Spectrum of Tetramethylsuccinonitrile
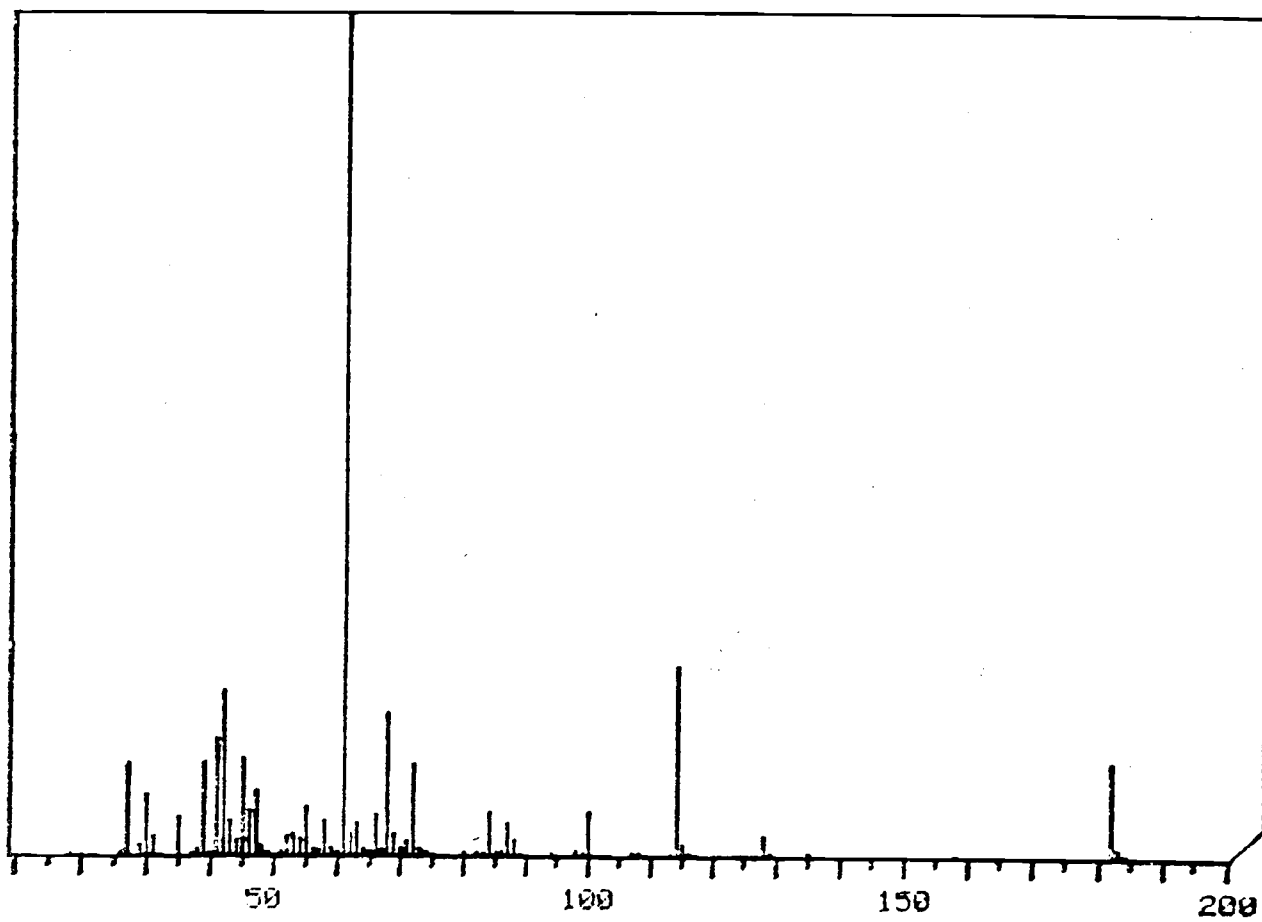
Ill. 3. Mass Spectrum of 1-(methylthiol-2, 3-dicyano-2, 3-dimethylbutane

Ill. 4. GC Traces of Aldicarb after Photolysis for 0, 3, and 6 hr.
A = Methylamine; B = Dimethyldisulfide; C = 2-methyl-2-
methylthiopropanenitrile; D = Tetramethylsuccinonitrile;
E = 2-methyl-2-methylthiopropanal oxime; F = 1-(methyl-
thio)-2, 3-dicyano-2, 3-dimethylbutane.
Analysis on column D on a FID GC

yield. A slightly better yield was obtained with acetophenone (0.33 M, Hanovia, corex). The yield of the 4 major products in benzonitrile (0.39 M, Hanovia, corex) was much higher.

Photolysis of O-(methylcarbamoyl)-isobutraldoxime in Acetonitrile

Irradiation (Hanovia, quartz) of a solution of O-(methyl-carbamoyl)-isobutyraldoxime (0.5 g, 0.0035 mol) in 25.0 ml of acetonitrile for periods up to 6 hr produced no photochemical reaction. After 15 hr a small amount of reaction took place, but no products were identified by GC-MS on column D at 60-220°.

Photolysis of O-(methylcarbamoyl)-trimethylacetaldehyde Oxime (37) in Acetonitrile

O-(methylcarbamoyl)-trimethylacetaldehyde oxime (0.31 g, 0.0019 mol) in 10 ml of acetonitrile produced no photochemical reaction on irradiation (Hanovia, quartz) for periods up to 12 hr. After 24 hr analysis with GC-MS on column D at 60-220° showed one major peak. It was not identified.

Quantum Yield Studies of the Photoproducts of Aldicarb

Quantum yield studies were run on four 10 ml portions of a solution of aldicarb (3.8 g, 0.02 mol) in 100 ml of acetonitrile. These and four 10 ml portions of the actinometer (cyclopentanone) were

placed in quartz tubes, degassed by 4 freeze-thaw cycles at 1×10^{-5}

torr, and irradiated (Rayonet) for 6 hr.   Analysis was carried out by

comparison of peak areas of the products to standards on a TC-GC

with an integrator.   Because the retention times are so different for

the products, each prdduct had to be analyzed under different condi-

tions with a different standard.   Methylamine and dimethyldisulfide

were analyzed with column E at 70° with iso-amyl alcohol as the

standard.   Analysis of 2-methyl-2-methylthiopropanonitrile was

achieved on column F at 160° with cyclohexanol as standard.   For

tetramethylsuccinonitrile column F at 145° was used with decanol.

Analysis of 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane was per-

formed on column B at 240° with heptanoic acid as the standard.   The

actinometer was analyzed with column G at 120° with undecane as the

standard.   Cyclohexanol forms 4-pentenal on irradiation with a

quantum yield of 0.38 (51).   Calculations were done according to the

method of Calvert and Pitts (52).[1]   The amount of aldicarb that had

reacted was determined by UV spectroscopy.   Quantum yields were

---

[1]This is a simplified method of calculating quantum yields and
requires that all the light incident on the solution be absorbed by the
sample.   This is assumed to be true when the concentration of the
sample is great enough for Absorbance to equal 5 or

$$\frac{I_o}{I} = 10^5.$$

also determined for the reaction sensitized with benzonitrile (0.49 M,

Hanovia, corex). Quantum yield data is summarized in Table 1.

Quantitative Analysis of Nitrile Formation on the GC Column

Standard solutions of aldicarb (ca. 0.0012 M) in acetonitrile were

injected on the TC-GC with column F at 130°. The amount of nitrile

formed was determined by comparison of peak areas with cyclohexanol.

The data are listed in Table 2. The 2-methyl-2-methylthiopropane-

nitrile observed in the photochemical reactions is formed by thermal

decomposition of aldicarb on the GC column.

Table 2. Pyrolysis of Aldicarb on the GC Column

Sample	Percent pyrolysis	Percent observed in photolysis
1	44.1	47.5
2	47.8	45.5
Average	46.0	46.5

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