

Photochemistry of Oxime Carbamates. 1. Phototransformations of Aldicarb

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The irradiation of aldicarb (1) in acetonitrile at 254 nm produced methylamine, dimethyl disulfide, tetramethylsuccinonitrile, and 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane as major products, with accompanying minor amounts of *N,N'*-dimethylurea. Photolyses carried out in the presence of benzophenone or acetophenone or benzonitrile generated the same product components. Analysis of the irradiations of related model oxime carbamates 2-methylpropanal *O*-[(methylamino)carbonyl]oxime (9) and 2,2-dimethylpropanal *O*-[(methylamino)carbonyl]oxime (10) revealed no photochemical transformations during a time period that exceeded that employed with aldicarb. Quantum yields for the direct and benzonitrile sensitized irradiations were measured. The photochemistry is interpreted in terms of an initial photodesmotic transition followed by intersystem crossing with the triplet state (³I) undergoing principally N-O or C-S bond fission with a minor role for carbamoyl-oxygen cleavage.

An interest in the photochemical transformations of oxime carbamates, a class of effective acetylcholinesterase inhibitors (Durden and Weiden, 1974; Fridinger et al., 1971; Friedman and Gemrich, 1971; Fukuto et al., 1969; Magee and Lempel, 1977), provided the impetus for an investigation of 2-methyl-2-(methylthio)propanal *O*-[(methylamino)carbonyl]oxime, aldicarb (1) (Payne et al., 1966), which is a contact poison and plant systemic insecticide for a variety of insect species.

EXPERIMENTAL SECTION

Melting points were obtained on a Büchi melting point apparatus and are uncorrected. A Varian HA-100 was used to record the nuclear magnetic resonance (NMR) spectra at 100 MHz. Infrared spectra (IR) were obtained with a Perkin-Elmer 727B infrared spectrometer. A Cary 15 spectrophotometer was used to record the ultraviolet (UV) spectra. Mass spectra were recorded on an Atlas CH7 mass spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Az. Vapor-phase chromatographic 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 ft × 1/8 in. o.d. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60-80 mesh; (B) 4 ft × 1/4 in. o.d. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60-80 mesh; (C) 10 ft × 1/8 in. o.d. 8% OV-101 aluminum column on Chromosorb Q, 100-120 mesh; (D) 4 ft × 1/8 in. o.d. 5% Carbowax 20M and 10% DC 200 on Chromosorb G NAW, 60-80 mesh; (E) 10 ft × 1/8 in. o.d. 5% Carbowax 20M and 10% DC 200 aluminum column on Chromosorb G NAW, 60-80 mesh; (F) 10 ft × 1/4 in. o.d. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60-80 mesh; (G) 12 ft × 1/4 in. o.d. 5% OV-17 aluminum column on Chromosorb Q, 100-120 mesh. Product quantities for quantum yields were calculated from chromatographic data based on relative peak areas measured with a Hewlett-Packard 3373 B integrator. Photolyses were carried out with Rayonet 2537-Å mercury lamps or a Hanovia 450-W high-pressure mercury lamp fitted with several filters. Quantum yields were run in a merry-go-round apparatus using either lamp.

Hydrolysis of 2-Methyl-2-(methylthio)propanal *O*-[(Methylamino)carbonyl]oxime (1) to 2-Methyl-

2-(methylthio)propanal Oxime (8). The method of Payne et al. (1966) was adapted for use in this laboratory. Sodium hydroxide (1.0 g, 0.025 mol) and 2-methyl-2-(methylthio)propanal *O*-[(methylamino)carbonyl]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 h, neutralized to pH 7 with dilute hydrochloric acid, and extracted with 4 × 10 mL of isopropyl ether. The ether was removed by distillation at aspirator pressure to yield 1.85 g (82%) of the oxime: NMR (CDCl₃, 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 *m/e* 133.

Preparation of Isobutyraldehyde *O*-[(Methylamino)carbonyl]oxime (9). 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 methyl isocyanate were added slowly and the solution was stirred for 20 h. The solvent and excess methyl isocyanate were removed by distillation at room temperature and aspirator pressure. Column chromatography of a 4 in. × 2 in. silica gel column with chloroform as eluent was used to purify the syrupy residue. The product was collected and the solvent removed on a rotoevaporator to give 8.0 g (66%) of isobutyraldehyde *O*-[(methylamino)carbonyl]oxime with mp 70-73 °C: NMR (CDCl₃, 100 MHz) δ 7.7 and 7.3 (1 H), 6.6 (1 H), 2.9-2.7 (3 H), 2.7-2.4 (1 H), 1.2-1.0 (6 H); IR (film) ν 1730 (C=O stretching), 1660 (C=N stretching) cm⁻¹; mass spectrum *m/e* 144.

Preparation of Trimethylacetaldehyde *O*-[(Methylamino)carbonyl]oxime (10). 2,2,2-Trimethylacetaldehyde oxime (4.4 g, 0.043 mol) was dissolved in 15 mL of acetonitrile in a three-necked flask under nitrogen. Methyl isocyanate (3.8 g, 0.066 mol) and 5 drops of triethylamine were added dropwise. The solution was stirred 21 h at 0 °C in an ice bath. Removal of the solvent and excess methyl isocyanate at 20 °C and aspirator pressure left a residue that was refrigerated overnight in a small portion of acetonitrile. The crystalline product was filtered with a Büchner funnel to give 3.9 g (58%) with mp 76-77 °C: NMR (CDCl₃, 100 MHz) δ 7.6 (1 H), 6.1 (1 H), 2.9 (3 H), 1.2 (9 H); IR (film) ν 1730 (C=O stretching), 1640 (C=N stretching) cm⁻¹; mass spectrum *m/e* 158. Anal. Calcd for C₇H₁₄N₂O₂: C, 53.13; H, 8.94. Found: C, 53.05; H, 8.68.

Photolysis of Aldicarb (1) in Water. Aldicarb (3.5 g, 0.10 mol) was dissolved in 500 mL of water in a large reaction flask. The solution was degassed by bubbling nitrogen through it for 1 h and irradiated (450-W Hanovia mercury lamp) through quartz for 5 h. The resultant

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yellow solution was continuously extracted with 500 mL of ether for 72 h. The ether layer was concentrated to 25 mL and analyzed by GC-MS using column A at 100–190 °C. 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 (5%) and dimethyl disulfide (5%), respectively. NMR and IR spectra were also obtained on peak 8 by preparative gas chromatography (GC) and it was identified as 2-methyl-2-(methylthio)propanenitrile: NMR (CDCl_3 , 100 MHz) δ 2.35 (3 H, singlet, $\text{CH}_3\text{-S}$), 1.7 [6 H, singlet, $(\text{CH}_3)_2\text{-C}$]; IR (neat) ν 2210 ($\text{C}\equiv\text{N}$ stretching) cm^{-1} ; mass spectrum m/e 115.

Photolysis of Isobutyraldehyde *O*-[(Methylamino)carbonyl]oxime (9). A solution of isobutyraldehyde *O*-[(methylamino)carbonyl]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 h. This solution was continuously extracted with ether for 72 h. The ether layer was concentrated and analyzed by GC-MS on column A at 100–175 °C. Minor photochemical reaction was observed, but the extent of reaction was too limited for product identification. Irradiation (Hanovia, quartz) of a solution of carbamate 10 (0.5 g, 0.0035 mol) in 25.0 mL of acetonitrile for periods up to 15 h produced no photochemical reaction. After 15 h a small amount of reaction appears to have taken place, but the extent was too limited for product identification.

Photolysis of Aldicarb (1) 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 of acetonitrile was placed in a resealable quartz tube degassed by five repeated freeze-thaw cycles at 1×10^{-5} torr. Irradiation was carried out with 2537-Å light (Rayonet) for 6 h, and the photoproducts were analyzed by GC-MS with two columns. Column A at 90 °C provided evidence for four components. The first peak was identified as methylamine by comparison with a published mass spectrum (Stenhagen et al., 1969). Peaks 2–4 were very small and were not identified. Fourteen components were observed on column D at 60–180 °C. Peak 2 was the solvent acetonitrile; peaks 1, 7, 8, and 12–14 were small and were not identified; peaks 3 and 9 were identified as dimethyl disulfide and *N,N*-dimethylurea (Grasseli, 1973). Gas chromatographic and mass spectral comparison with authentic samples proved that peaks 6 and 11 were 2-methyl-2-methylthiopropional 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-(methylthio)propanenitrile by comparison with a known standard. Comparison of the spectrum of an authentic sample with peak 5 proved it to be tetramethylsuccinonitrile. 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, $-\text{CH}_2-$), 2.3 (3 H, $\text{CH}_3\text{-S}$), 1.6 (3 H, $\text{CH}_3\text{-C-CH}_2\text{-S-}$), 1.5 [6 H, $(\text{CH}_3)_2\text{-C-}$]; IR (neat) ν 2240 (CN stretching) cm^{-1} ; mass spectrum m/e 182.

Photolysis of Aldicarb (1) 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 h. Analysis on column D at 60–180 °C showed 2-methyl-2-(methylthio)propanenitrile and 2-methyl-2-(methylthio)propanal oxime decreased with time, while methylamine, dimethyl sulfide, tetramethylsuccinonitrile, and 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane increased with time.

Table I. Quantum Yield for the Photodecompositions of Aldicarb

compound	quantum yield	SD	% yield
Unsensitized Reaction ^a			
2	0.93	0.13	54
3	0.55	0.027	63
4	0.062	0.0064	7.2
5	0.024	0.0052	4.4
Sensitized Reaction ^b			
2	0.89		53
3	0.12		15
4	<i>c</i>		<i>c</i>
5	0.017		2.1

^a Average of four runs. ^b Average of two runs. ^c Sensitizer hindered analysis of this component.

Photolysis of Aldicarb (1) with Sensitizers. Aldicarb was irradiated with three sensitizers by using the same general procedure as above. Benzophenone (0.30 M, Hanovia, Pyrex) produced the same major products as the unsensitized reaction in low yield. A slightly better yield was obtained with acetophenone (0.33 M, Hanovia, Corex). The yield of the four major products in benzonitrile (0.39 M, Hanovia, Corex) was much higher.

Photolysis of Trimethylacetaldehyde *O*-[(Methylamino)carbonyl]oxime (10). Trimethylacetaldehyde *O*-[(methylamino)carbonyl]oxime (0.31 g, 0.0019 mol) in 10 mL of acetonitrile produced no photochemical reaction on irradiation (Hanovia, quartz) for periods up to 15 h. After 24 h, analysis with GC-MS on column D at 60–220 °C showed one major peak, present in too limited an extent for identification.

Quantum Yield Studies of the Photoproducts of Aldicarb (1). 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 four freeze-thaw cycles at 1×10^{-5} torr, and irradiated (Rayonet) for 6 h. Analysis was carried out by comparison of peak areas of the products to standards on a thermal conductivity gas chromatograph with an integrator. Because the retention times are so different for the products, each product had to be analyzed under different conditions with a different standard, which was added subsequent to the irradiation. Methylamine and dimethyl disulfide were analyzed with column E at 70 °C with isoamyl alcohol as the standard. Analysis of 2-methyl-2-(methylthio)propanenitrile was achieved on column F at 160 °C with cyclohexanol as the standard. For tetramethylsuccinonitrile column F at 145 °C was used with decanol. Analysis of 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane was performed on column B at 240 °C with heptanoic acid as the standard. The actinometer was analyzed with column G at 120 °C with undecane as the standard. Cyclopentanone forms 4-pentanal on irradiation with a quantum yield of 0.38 (Dunion and Trumbore, 1965). Calculations were done according to the method of Calvert and Pitts (1966) (with $I_0/I > 10^5$). The amount of aldicarb that had reacted was determined by UV spectroscopy. Quantum yields were also determined for the reaction sensitized with benzonitrile (0.49 M, Hanovia, Corex). Quantum yield data are summarized in Table I.

RESULTS AND DISCUSSION

Our initial approach was to evaluate the photodecomposition of aldicarb (1) and related oxime carbamates in dilute aqueous solutions. Photolysis of aldicarb in water (medium-pressure mercury lamp) for a period of 5 h resulted in a product mixture containing α -methylacrylo-

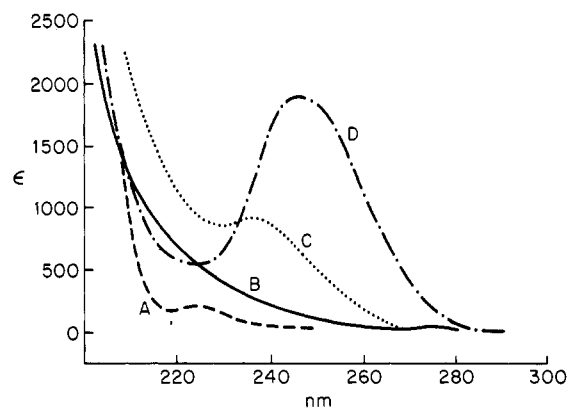
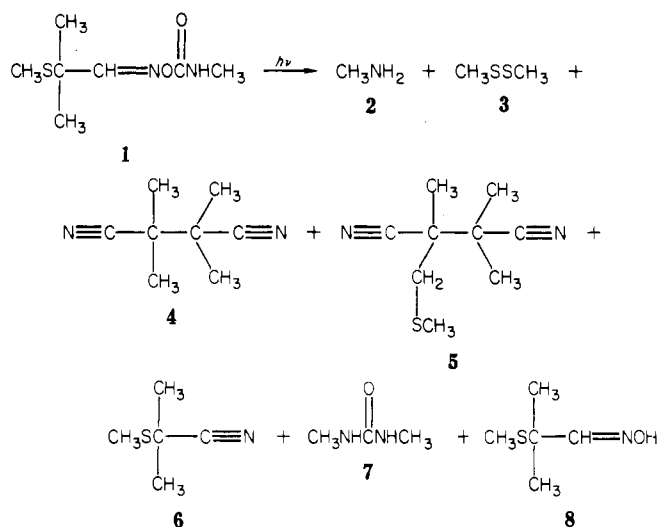
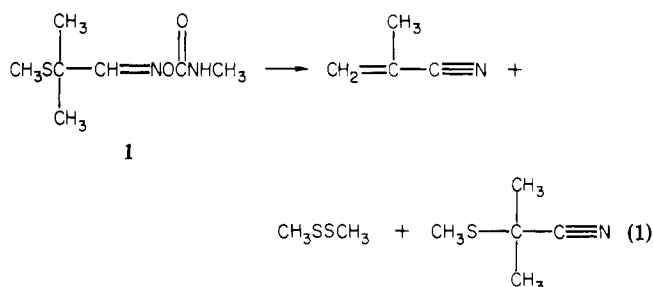


Figure 1. Ultraviolet spectra in acetonitrile: (A) 2-methylpropanal *O*-[(methylamino)carbonyl]oxime; (B) 2,2-dimethylpropanal *O*-[(methylamino)carbonyl]oxime; (C) 2-(methylthio)-2-methylpropanal oxime; (D) 2-(methylthio)-2-methylpropanal *O*-[(methylamino)carbonyl]oxime.

Scheme I



nitrile, dimethyl disulfide, and 2-(methylthio)-2-methylpropanenitrile (eq 1). Due to the multiplicity of products

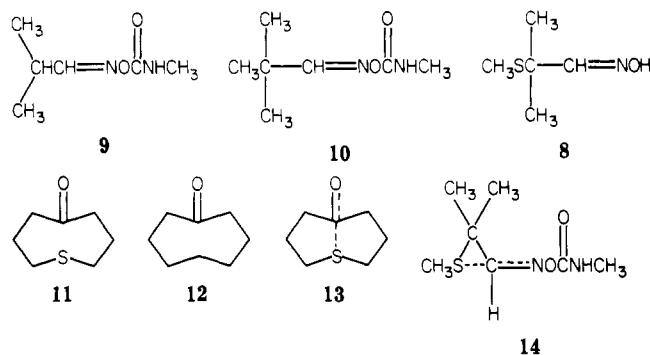


formed in addition to those specified in eq 1 and additional problems of an analytical nature, the range of conditions was expanded to include photolyses carried out in acetonitrile, where direct analysis of the irradiated solution was possible.

Irradiation of solutions of aldicarb in acetonitrile at 254 nm for periods ranging from 1 to 6 h revealed that the major products are methylamine (2), dimethyl disulfide (3), tetramethylsuccinonitrile (4), and 1-(methylthio)-2,3-dicyano-2,3-dimethylbutane (5) (Scheme I). 2-(Methylthio)-2-methylpropanenitrile (6) and oxime (8) were observed by gas chromatographic analysis, but additional experimentation demonstrated that they were produced thermally during the analysis; *N,N'*-dimethylurea (7) was

formed but was a minor component of the product mixture. Reactions using benzophenone ($\lambda > 300$ nm), acetophenone ($\lambda > 270$ nm), and benzonitrile ($\lambda > 270$ nm) as the sensitizer generated the same array of products (2–5 and 7) as in the unsensitized process at 254 nm.

In order to gain some insight into these phototransformations, two model substrates were prepared and irradiated. Surprisingly, 2-methylpropanal *O*-[(methylamino)carbonyl]oxime (9) and 2,2-dimethylpropanal *O*-[(methylamino)carbonyl]oxime (10) exhibited no photochemical transformations with irradiation for periods up to 15 h. The ultraviolet spectra (Figure 1) provide a basis for an explanation of this lack of reactivity. Since sulfides normally exhibit λ_{max} values that are less than 230 nm with ϵ values less than 400 (Calvert and Pitts, 1966) and model systems 9 and 10 show no maxima above 230 nm, the λ_{max}

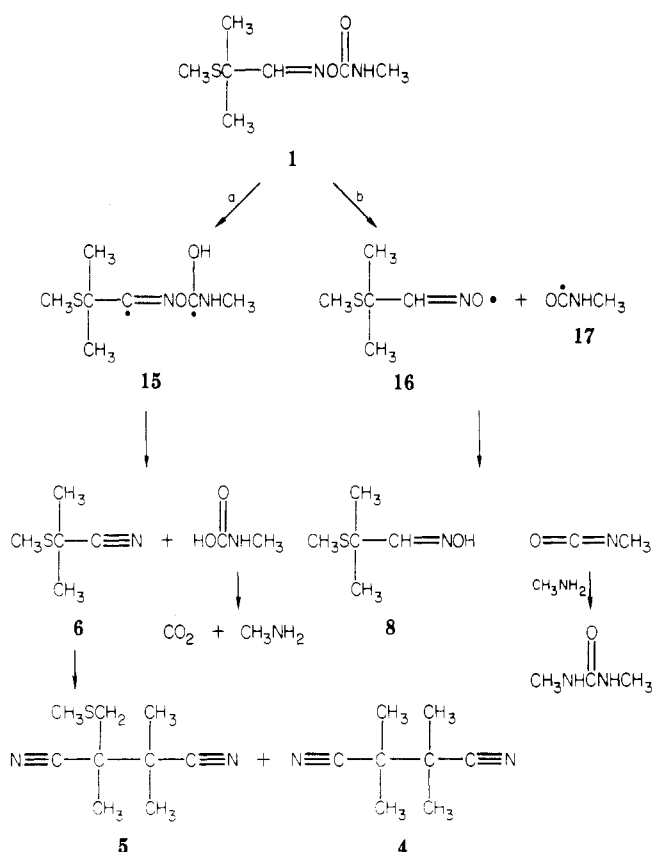


values for oxime 8 and aldicarb (1) at 235 and 245 nm, respectively, are clearly enhanced due to the combination of functional groups present. We ascribe this enhancement to a photodesmotic effect that has been observed with cyclic unsaturated ketones (Kosower et al., 1961) and cyclic γ -keto sulfides (Johnson and Berchtold, 1967, 1970). For example, 1-thiacyclooctan-5-one (11) has a λ_{max} of 227 nm with an ϵ of 2884 (cyclohexane), whereas cyclohexanone (12) has no λ_{max} over 200 nm (with the exception of a normal $n-\pi^*$ band at 288 nm) (Leonard and Johnson, 1962). This is explained by transannular interaction between the sulfur and carbonyl (13) in the excited state. A similar interaction between the sulfur and the imine double bond (14) might very well enhance the λ_{max} and ϵ values in 8 and 1.

Quantum yield data reinforce the developing mechanistic picture. Quantum yields for the major products resulting from the direct irradiation in acetonitrile and the benzonitrile-sensitized run in acetonitrile are presented in Table I.

These results strongly suggest that the triplet state of aldicarb ($^3\mathbf{1}$) is the key intermediate and that nitrogen-oxygen and carbon-sulfur cleavage is the major pathway, while carbamoyl-oxygen cleavage is a minor reaction pathway. Nitrogen-oxygen cleavage finds precedence in the photolytic cleavage of *O*-alkyl and *O*-acyl oximes (Ishikawa et al., 1975; Ohta and Tokumaru, 1975; Padwa, 1977; Pfoertner and Foricher, 1982; Sato et al., 1972; Vermes and Beugelmans, 1969; Yoshida et al., 1975), while carbamoyl-oxygen fission is similar to the acyl-oxygen cleavage noted for the photodecomposition of *O*-acyl oximes of steroidal ketones (Beugelmans and Vermes, 1971; Vermes and Beugelmans, 1969). The nitrogen-oxygen cleavage pathway might well involve intramolecular abstraction of the imine hydrogen forming diradical 15. Intersystem crossing followed by N–O fission leads to nitrile 6 and *N*-methylcarbamic acid, which upon decarboxylation produces methylamine and carbon dioxide. Photochemical fission of nitrile 6 appears to be a very reasonable route to dinitriles 4 and 5 (pathway a, Scheme

Scheme II

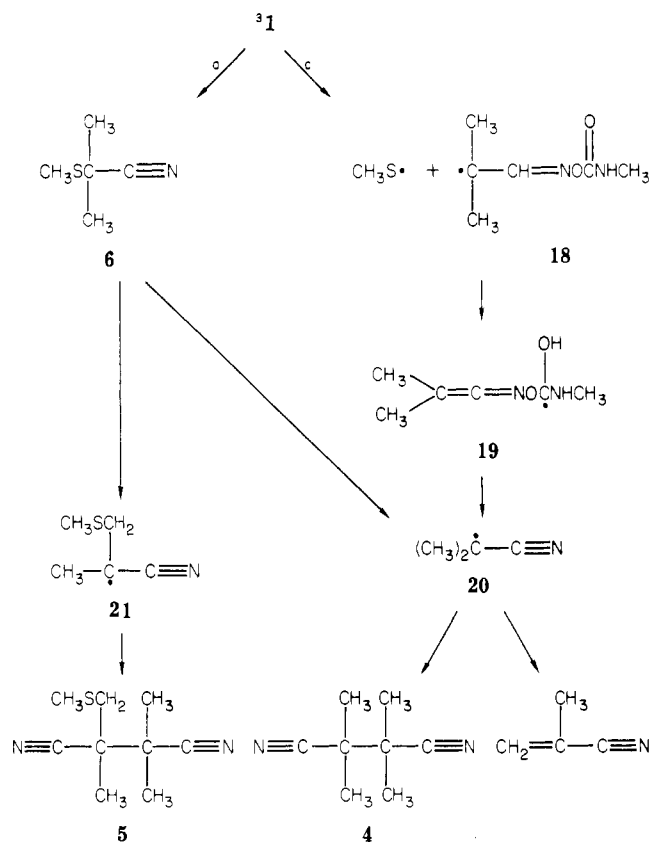


II). Alternatively, carbamoyl-oxygen cleavage of $^3\text{1}$ would generate radicals 16 and 17, which could, within a solvent cage, produce oxime 8 and methyl isocyanate. The reaction of methyl isocyanate with methylamine yields *N,N'*-dimethylurea (pathway b, Scheme II).

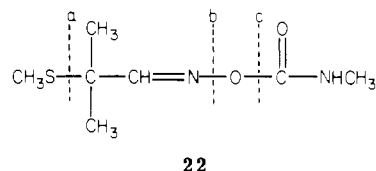
A mechanistic view of the conversion of nitrile 6 to dinitriles 4 and 5 is presented in Scheme III. Hydrogen abstraction from 6, with anchimeric assistance by a bridging methylthio group (Skell and Shea, 1973; Readio and Skell, 1966; Block, 1978), could lead directly to α -cyano radical 21, which combines with α -cyano radical 20 to form dinitrile 5. Radical 20 might be formed by photochemical C-S bond homolysis of nitrile 6 or by pathway c, which is an alternative to pathway a differing only in the timing of N-O and C-S bond fission processes. In pathway c C-S bond fission is followed by intramolecular hydrogen abstraction generating 19 which then undergoes N-O fission to produce α -cyano radical 20. Isobutyronitrile radical 20 (the AIBN radical) would be expected to have a long enough lifetime to combine with 21 to form unsymmetrical dinitrile 5 or to dimerize forming tetramethylsuccinonitrile 4 (Leermakers et al., 1966). α -Methylacrylonitrile, which is formed in aqueous media, is also a logical end product from 21 [thiyl radical addition to alkenes is known to be reversible (Abell, 1973)] and from 20 in a hydrogen atom transfer process.

In summary, ultraviolet spectral analysis of aldicarb (1) and 2-(methylthio)-2-methylpropanal oxime (8) and model *O*-[(methylamino)carbonyl]oximes 9 and 10 reveals enhanced values for λ_{max} and molecular absorption coefficient ϵ for 1 and 8, which is due to a photodesmotic transition resulting from the homoconjugate placement of sulfur and imine functional groups. We find, however, no clear evidence of the photodesmotic transition in the photofragmentations uncovered. Sensitized irradiations provide evidence for the triplet state of aldicarb ($^3\text{1}$) as the key reactive intermediate, while a mechanistic analysis of the

Scheme III



photofragmentations that occur provides evidence of fission of C-S, N-O, and carbamoyl-oxygen bonds (homolysis at points a-c in 22).



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Registry No. 1, 116-06-3; 2, 74-89-5; 3, 624-92-0; 4, 3333-52-6; 5, 90695-74-2; 6, 10074-86-9; 7, 96-31-1; 8, 1646-75-9; 9, 10520-38-4; 10, 6062-02-8; benzophenone, 119-61-9; acetophenone, 98-86-2; benzonitrile, 100-47-0; isobutyraldehyde oxime, 151-00-8; triethylamine, 121-44-8; methyl isocyanate, 624-83-9; 2,2,2-trimethylacetaldehyde oxime, 637-91-2.

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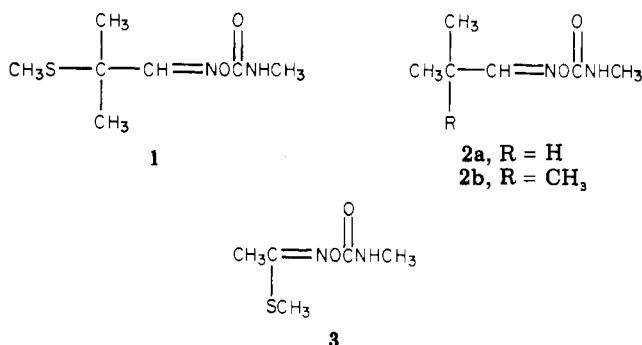
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Photochemistry of Oxime Carbamates. 2. Phototransformations of Methomyl

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The irradiation of methomyl in dilute aqueous solution at 254 nm formed acetonitrile, dimethyl disulfide, acetone, *N*-ethylidenemethylamine, and carbon dioxide. Irradiation in tetrahydrofuran produced carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4) as major products, with acetone, dimethylamine, *N,N*'-dimethylurea, dimethyl sulfoxide, methyl thioacetate (5), and methomyl oxime (6) as minor products. Irradiation of methomyl in the presence of benzophenone sensitizer in THF at 254 nm results in the formation of carbon dioxide, methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4). Irradiation in THF in the presence of acetophenone generated carbon dioxide, methylamine, acetonitrile, and dimethyl disulfide, while irradiation in THF in the presence of benzonitrile produced methylamine, acetonitrile, dimethyl disulfide, and biacetyl bis(methylhydrazone) (4). The quenching effects on the quantum yields of photoproducts using isoprene as the triplet-state quencher were measured, providing a linear Stern-Volmer plot. The mechanistic implications of these results are discussed.

Our earlier study on the photochemistry of aldicarb (1)



and related model oxime carbamates (2a,b) (Freeman and McCarthy, 1984) led us to a consideration of the phototransformations of the closely related methomyl, methyl *N*-[[[(methylamino)carbonyl]oxy]ethanimidothioate (3). To the best of our knowledge there have been no reports in the literature on the photochemistry of methomyl other than the very recent study of Koshy et al. (1983), which focused principally on the photodecomposition of a thio-phosphoramidate derivative of methomyl.

EXPERIMENTAL SECTION

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 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 ft \times 1/4 in. o.d. 5% Carbowax 20M aluminum column on Chromosorb G NAW, 60-80 mesh; (B) 20 ft \times 1/8 in. o.d. 5% Carbowax 20 M aluminum column on Chromosorb W AW, 60-80 mesh; (C) 15 ft \times 1/8 in. o.d. 10% Carbowax 20 M-2% KOH copper column on Anakrom ABS, 70-80 mesh; (D) 5 ft \times 1/8 in. o.d. 10% Carbowax 1500 aluminum column on Chromosorb W, 60-80 mesh; (E) 19 ft \times 1/8 in. o.d. 20% Carbowax 20 M aluminum column on Anakrom ABS, 70-80 mesh; (F) 2 m \times 1/8 in. o.d. 10% Dinonyl phthalate aluminum column on Chromosorb W AW DMCS, 80-100 mesh, for Varian Series 1200 chromatograph; (H) 10 ft \times 1/8 in. o.d. 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 by 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, 4.6-mm i.d.; column packing, Lichrosorb silica; particle size and frit, 5 and 0.5 μm , respectively; flow rate 1 mL/min; solvent system, dichloromethylene (DCM)-methanol-isooctane (TMP). For reversed-phase HPLC analysis a 50:50

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