

LITERATURE CITED

- Curley, A., Burse, V. W., Grim, M. E., Jennings, R. W., Linder, R. E., *Environ. Res.* 4, 481 (1971).
- Daniels, L. B., Campbell, J. R., Martz, F. A., Hedrick, H. B., *J. Anim. Sci.* 30, 593 (1970).
- Dinius, D. A., Oltjen, R. R., *J. Anim. Sci.* 33, 1344 (1971).
- Dinius, D. A., Oltjen, R. R., *J. Anim. Sci.* 34, 137 (1972).
- Edwards, R., *Chem. Ind. (London)*, 1340 (1971).
- Environmental Health Perspectives, National Institute of Environmental Health Sciences, Research Triangle Park, N. C., Experimental Issue No. 1, April, 1972.
- Food Chem. News*, 41 (Nov 22, 1971).
- Fries, G. F., Marrow, G. S., *J. Ass. Offic. Anal. Chem.* 56, 1002 (1973).
- Fries, G. F., Marrow, G. S., Jr., Gordon, C. H., *Bull. Environ. Contam. Toxicol.* 7, 252 (1972).
- Fries, G. F., Marrow, G. S., Jr., Gordon, C. H., *J. Agr. Food Chem.* 21, 117 (1973).
- Goering, F., Van Soest, P. J., U. S. Department of Agriculture Handbook No. 379, 1970.
- Grant, D. L., Phillips, W. E. J., Villeneuve, D. C., *Bull. Environ. Contam. Toxicol.* 6, 102 (1971).
- Gutenmann, W. H., Lisk, D. J., *J. Agr. Food Chem.* 8, 306 (1960).
- Hankin, L., Heichel, G. H., Botsford, R. A., *Clin. Pediat.* 12, 654 (1973).
- Hatch, W. R., Ott, W. L., *Anal. Chem.* 40, 2085 (1968).
- Kesler, E. M., Chandler, P. T., Branding, A. E., *J. Dairy Sci.* 50, 1994 (1967).
- Levi, I., Nowicki, T. W., *Bull. Environ. Contam. Toxicol.* 7, 133 (1972).
- Masuda, Y., Kagawa, R., *Nature (London)* 237, 41 (1972).
- Mertens, D. R., Campbell, R. R., Martz, F. A., Hilderbrand, E. S., *J. Dairy Sci.* 54, 667 (1971a).
- Mertens, D. R., Martz, F. A., Campbell, J. R., *J. Dairy Sci.* 54, 931 (1971b).
- Mertens, D. R., Van Soest, P. S., *J. Anim. Sci.* 54, 778 (1971).
- Millett, M. A., Baker, A. J., Satter, L. D., McGovern, J. N., Dinius, D. A., *J. Anim. Sci.* 37, 599 (1973).
- Nishimuta, J. F., Sherrod, L. B., Furr, R. D., Hansen, K. R., *J. Anim. Sci.* 29, 642 (1969).
- Peakall, D. B., *Residue Rev.* 44, 1 (1972).
- Peakall, D. B., Lincer, J. L., *BioScience* 20, 958 (1970).
- Pesticide Analytical Manual, Vol. 1, U.S. Department of Health, Education and Welfare, Food and Drug Administration, Washington, D.C., revised, 1971, Sections 211.13h, 211.14a, and 211.14d.
- Platonow, N., Chen, N. Y., *Vet Rec.*, 69 (Jan 20, 1973).
- Platonow, N. S., Funnell, H. S., Bullock, D. H., Arnott, R., Saschenbrecker, P. W., Grieve, D. G., *J. Dairy Sci.* 54, 1305 (1971).
- Price, N. O., Young, R. W., Dickinson, J. K., *Proc. Soc. Exp. Biol. Med.* 139, 1280 (1972).
- Rook, J. A. F., Campling, R. C., *J. Agr. Sci.* 53, 330 (1959).
- Saschenbrecker, P. W., Funnell, H. S., Platonow, N. S., *Vet. Rec.*, 100 (Jan 22, 1972).
- Schroeder, H. A., Air Quality Monograph #70-12, American Petroleum Institute, Washington, D.C., 1970.
- Schroeder, H. A., Balassa, J. J., Gibson, F. S., Valanjü, S. N., *J. Chronic Dis.* 14, 408 (1961).
- Serum, J. W., Tong, S. C., St. John, L. E., Jr., Bache, C. A., Mertens, D. R., Lisk, D. J., *Bull. Environ. Contam. Toxicol.* 10, 88 (1973).
- Shahied, S. I., Stanovick, R. P., McInturff, D. E., Missaghi, E., *Bull. Environ. Contam. Toxicol.* 10, 80 (1973).
- Sherrod, L. B., Hansen, K. R., *J. Anim. Sci.* 36, 592 (1973).
- Skrentny, R. F., Hemken, R. W., Dorrough, H. W., *Bull. Environ. Contam. Toxicol.* 6, 409 (1971).
- Stanley, R. E., Mullen, A. A., Bretthauer, E. W., *Health Phys.* 21, 211 (1971).
- Stanovick, R. P., Shahied, S. I., Missaghi, E., *Bull. Environ. Contam. Toxicol.* 10, 101 (1973).
- Thomas, G. H., Reynolds, L. M., *Bull. Environ. Contam. Toxicol.* 10, 37 (1973).
- Thomas, J. W., Yu, Y., Hoffer, J. A., *J. Anim. Sci.* 31, 255 (1970).
- Truhaut, R., Berrod, F., *Ann. Pharm. Fr.* 20, 637 (1962).
- Villeneuve, D. C., Reynolds, L. M., Thomas, G. H., Phillips, W. E. J., *J. Ass. Offic. Anal. Chem.* 56, 999 (1973).
- Williams, G. F., Musgrave, S. D., Schuh, J. D., MacVicar, R. W., *J. Dairy Sci.* 41, 349 (1958).

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Photodecomposition of Methidathion

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Irradiation of methidathion was carried out with ultraviolet light of a wavelength of 254 m μ . The photoproducts were isolated and purified with different systems of tlc and by comparison of their infrared and mass spectra with the spectra of synthesized samples. The following products were identified: the P=O analog; *O,O,S*-trimethyldithiophosphonic acid; *O,O,S*-tri-

methylthiophosphonic acid; *O,O,O',O'*-tetramethyl-*S,S*-methylbis(dithiophosphonic) acid; 2-methoxy-4-methylthiomethyl- Δ^2 -1,3,4-thiadiazolin-5-one; 2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-one; 2-methoxy-4-methyldithiomethyl- Δ^2 -1,3,4-thiadiazolin-5-one; bis(2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-on-4-yl) disulfide; 1,3,4-oxodiazolidine-2,5-dione.

The fate of methidathion (Supracide, GS 13005, *O,O*-dimethyl 5-[(2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-on-4-yl)-methyl] phosphorodithioate), a Ciba-Geigy insecticide, has been studied in several biological systems. Esser and Müller (1966) and Esser *et al.* (1968) following the metabolic pathway in the rat and in plants showed an appreciable breakdown of the applied [5-carbonyl- 14 C]methidathion to 14 CO $_2$ (27.4% CO $_2$ after 14 days on beans, 31.6% CO $_2$ after 56 days on apples, and 80.5% after 4 days in rats).

Bull (1968), using labeled compounds on cotton, alfalfa, rats, and fifth instar tobacco budworms, concluded that in

insects and plants CO $_2$ was not a major end product of the metabolism of the heterocyclic ring and reported the presence of several water-soluble metabolites. Esser *et al.* (1968) identified three main metabolites in the rat: the 4-methylthiomethyl derivative of the intact heterocyclic ring and its oxidation products, the sulfoxide and the sulfone. Cassidy *et al.* (1969a,b), after treating alfalfa with methidathion, reported the presence of the oxygen analog and noncholinesterase inhibiting water-soluble 14 C residues. Polan *et al.* (1969), studying the physiological effects and the metabolism in the bovine, found very low levels of the parent compound in the tissues and no evidence for the presence of the oxygen analog. Rufenacht (1968) described the synthesis of methidathion and the possible metabolites. Analytical methods for routine determinations of residues in plants, fruits, and soils have been published by Eberle *et al.* (1967) and Mattson *et al.* (1969). Eberle *et al.* reported, besides methidathion,

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Table I. R_f Values of Methidathion and Its Breakdown Products on Silica Gel GF 254 Tlc Chromatograms

Product no.	Eluent					
	<i>n</i> -Hexane-ethyl ether		Benzene-ethyl acetate		Ethyl ether	Benzene
	70:30	30:70	60:40	Dichloromethane		
1	0.90	0.94	0.87	0.95	0.97	
2 and 11	0.63	0.90	0.74	0.85	0.96	
3	0.47	0.87	0.68	0.56		0.35
4	0.47	0.60	0.82			0.85
5	0.47	0.70	0.70			0.84
6		0.65	0.69	0.22	0.95	
7 and 12		0.28	0.26	0.10	0.42	
8		0.12	0.18	0.05	0.34	
9	0.23	0.75	0.52	0.12	0.96	
10	0.14	0.62	0.45	0.04	0.90	
Methidathion	0.57	0.78	0.65			

Table II. Ir Bands of Methidathion and Its Breakdown Products

cm ⁻¹		cm ⁻¹	
3200	NH	1300-1250	C—O (ring) and P=O
3000-2800	CH ₃ CH ₂	1180-1170	POCH ₃
1690-1600	C=O	1020	POCH ₃
1585	C=N	950	C—N (ring)
1450-1420	CH ₂	820	P=S
1410-1400	SCH ₂ N	650-640	P=S
1340	OCH ₃		

the presence of the oxygen analog and the heterocyclic moiety.

Besides the metabolic decomposition of organophosphorus insecticides, environmental factors can cause chemical transformations. The study of the effect of one of these, light, can therefore be of considerable interest for a full understanding of the disappearance routes and of the structure of possible transformation products. One of the most sensitive detection methods for organophosphorus insecticides is based on this nonmetabolic transformation of the parent compound to more polar products, usually the P=O analogs, which are more potent as AChE inhibitors.

The decomposition of organophosphorus insecticides under the influence of light has been studied by Cook (1954, 1955), Cook and Ottes (1959), Mitchell (1961), Mitchell *et al.* (1968), Yositaka *et al.* (1968), and others. They were generally agreed that the parent compounds were converted to transformation products but in most cases no attempt at characterization was made. In this work the effect of light on methidathion was studied and the most important transformation products were separated and identified.

MATERIALS AND APPARATUS

Chemicals. Methidathion (*O,O*-dimethyl 5-[2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-on-4-yl)methyl] phosphorodithioate) was received as a 100% pure product (mp 39-40°) from Ciba-Geigy A. G. Basel and was also prepared according to a procedure based on the one described by Rufenacht (1968). The P=O analog of methidathion and 2-methoxy-4-methylthiomethyl- Δ^2 -1,3,4-thiadiazolin-5-one were received from Ciba-Geigy A. G. Basel. Dithiophosphorus acid *O,O,S*-trimethyl ester was prepared from

methanol and phosphorus pentasulfide according to a procedure by Hoegberg and Cassaday (1951). 2-Methoxy- Δ^2 -1,3,4-thiadiazolin-5-one was prepared according to Rufenacht (1968).

Irradiation. The light source consisted of different lamps and sunlight: Westinghouse Sterilamp WL 782-L-30 with 90% of all energy in the 253.7-m μ band; Desaga Uvis lamp of 60 W and filters at 254 and 365 m μ ; high-pressure Hg lamp (Xenon) with approximately the wavelengths and twofold intensity of natural sunlight.

Gas Chromatography. Detection of methidathion was carried out on a Varian Aerograph Model Hy-Fi 600 instrument equipped with an electron capture detector and an alkali flame detector. The columns used (5 \times 1/8 in. Pyrex) were packed with either 5% Dow-Corning 11 or 2% QF₁ on 60-80 mesh Chromosorb W.

Thin-Layer Chromatography. Silica gel plates of 0.25 and 0.50 mm thicknesses were used for the separation and isolation of the decomposition products. The compounds were detected with ultraviolet (uv) light on silica gel GF 254 plates or with color reagents, based on palladium chloride, ninhydrin, or silver nitrate, and with an enzymatic method using beef liver homogenate as enzyme solution and potassium hexacyanoferrate or a diazonium salt solution as the color reagent.

Column Chromatography. Silica gel was used for column chromatography. The height of the column was 10 cm and the diameter 1 cm. Dichloromethane was used as eluent.

Infrared spectra were measured in KBr disks for solids or between NaCl disks for liquids with a Perkin-Elmer Model 257 infrared spectrophotometer.

Mass spectra were measured with a M.S.-9 spectrometer (AEI).

Nmr spectra were measured with a Varian 60-MHz nmr spectrometer in carbon tetrachloride or acetone-*d*-₆ or deuteriochloroform (2:1).

IRRADIATION AND PRODUCT ISOLATION

The product for irradiation was contained in 25-ml borosilicate glass beakers. A 0.5% solution of methidathion (5 mg) (1 ml) in acetone was added to different beakers and the irradiation started after the evaporation of the solvent. The lamps were centered over the beakers and the distance between the product and the lamps was 5-6 cm (Westinghouse and Desaga lamps) and \pm 1.5 m (Xenon lamp). For irradiation with sunlight the beakers were covered with a polypropylene film of 0.035 mm thickness and permeable to uv and visible light.

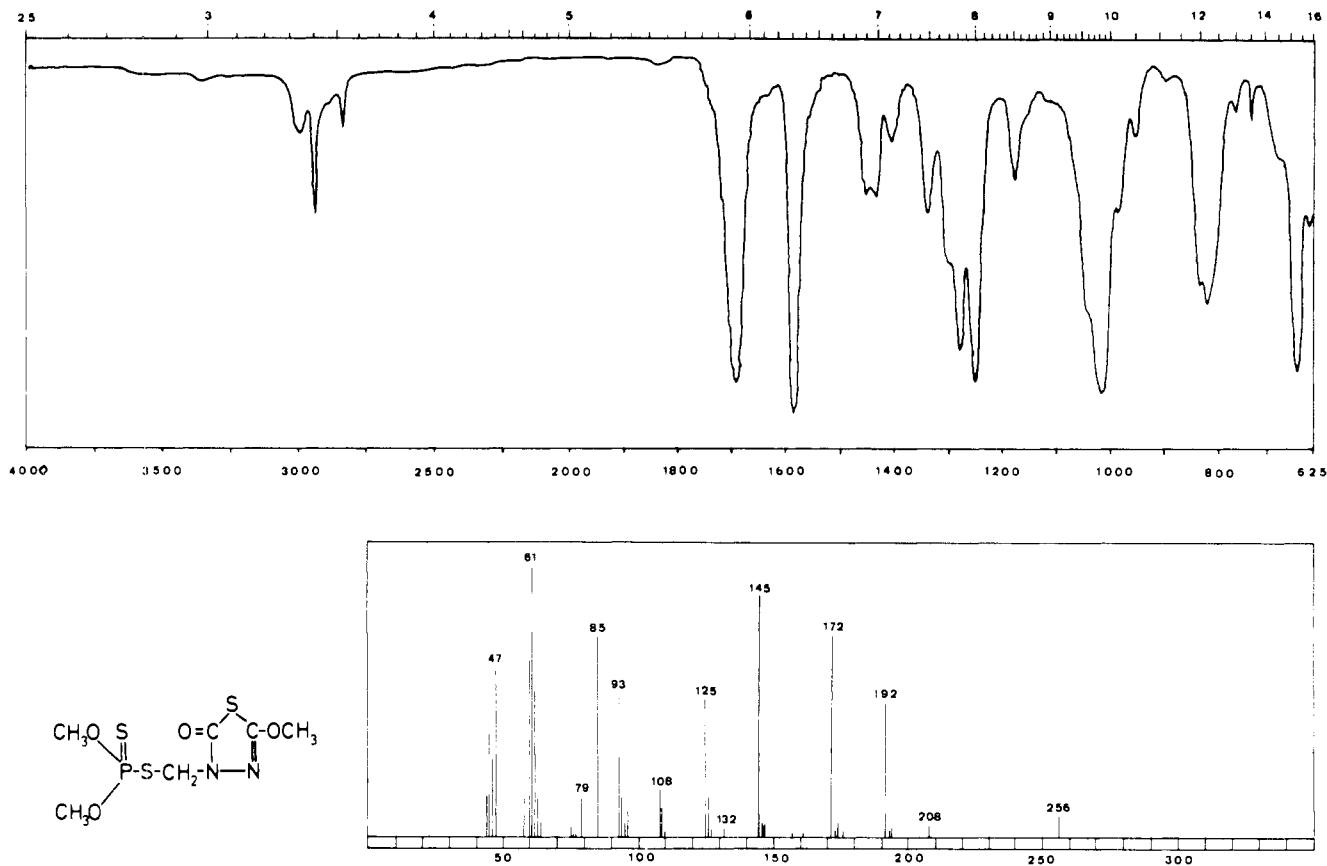


Figure 1. Infrared and mass spectra of methidathion.

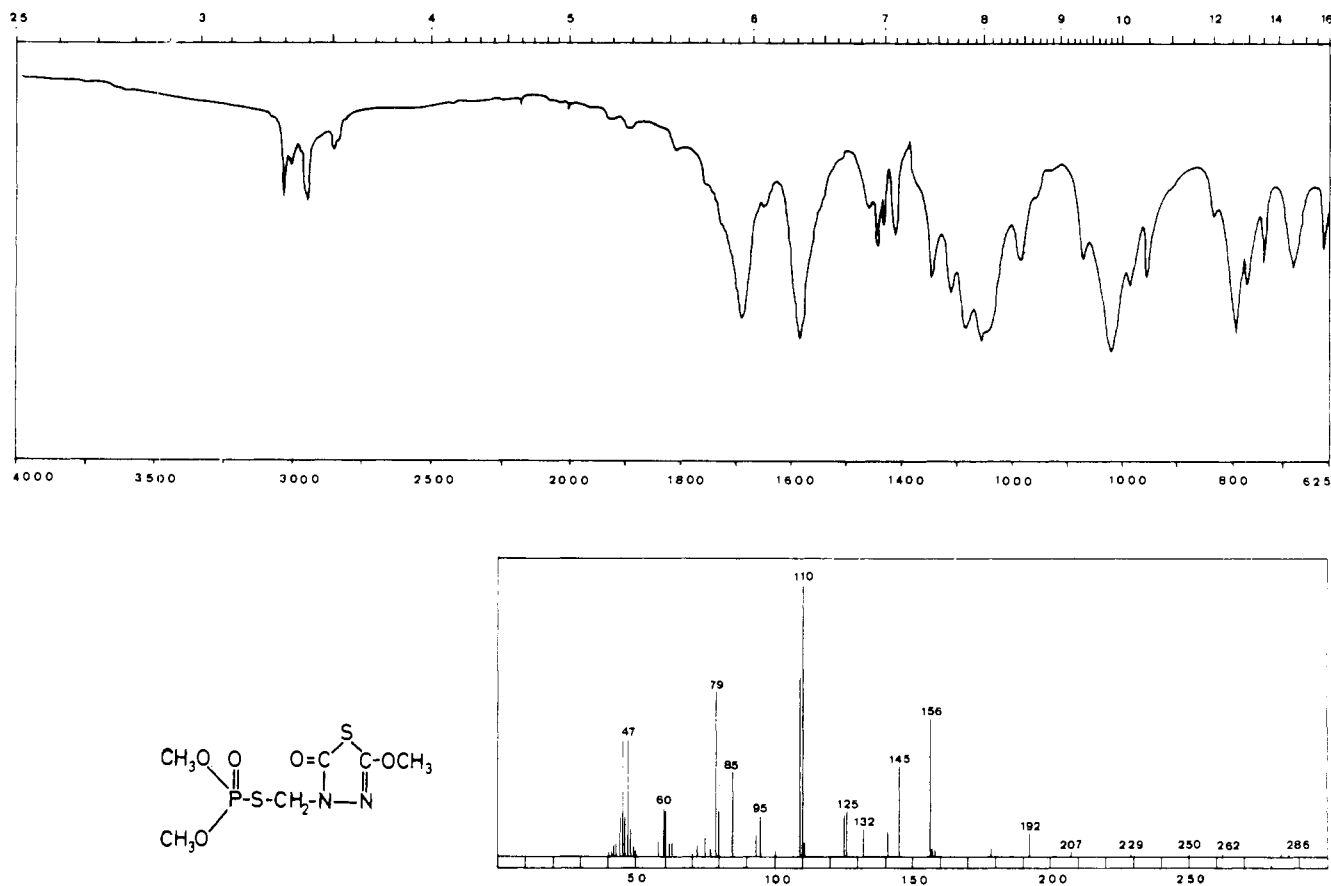


Figure 2. Infrared and mass spectra of *O,O*-dimethyl *S*-[(2-methoxy- Δ^2 -1,2-thiadiazolin-5-onyl)methyl] phosphorothiolate (product 8).

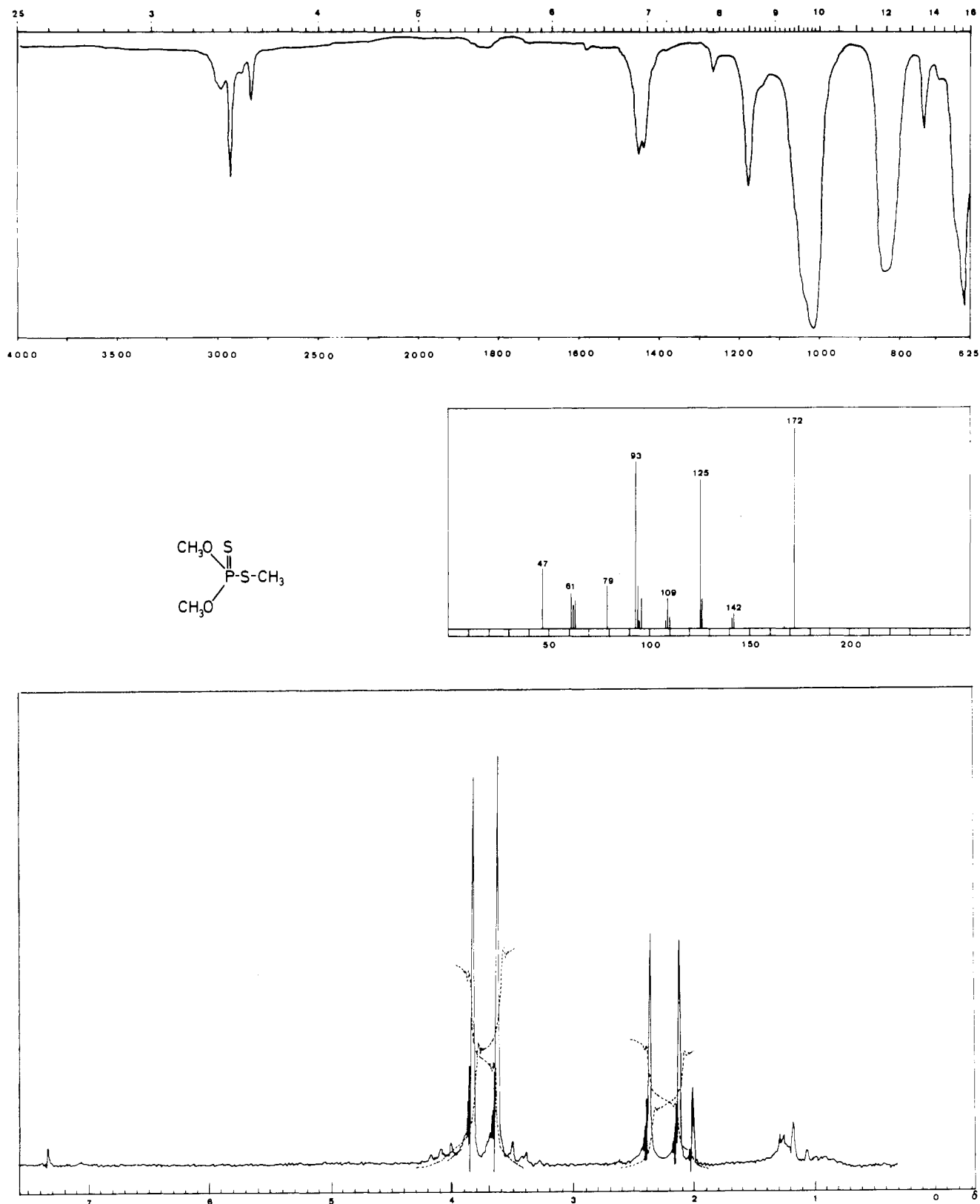


Figure 3. Infrared, mass, and nmr spectra of *O,O,S*-trimethyldithiophosphonic acid (product 2).

Most breakdown products were isolated using preparative tlc. The thus separated compounds were further purified by tlc using different solvent systems until a pure compound was obtained for structure determination. To obtain a sufficient quantity of material, 5 g of methidathion was irradiated with the Westinghouse lamp. The product was dissolved in acetone in a glass container of 18 × 8 cm and after evaporation of the solvent the oily film was irradiated for 3 days. The resulting brownish film still

contained about 15% unchanged methidathion. The oily mixture thus obtained was dissolved in a chloroform-water mixture, and the two layers were treated separately. The chloroform phase, after drying over anhydrous Na_2SO_4 , was evaporated to dryness using a rotavapor and redissolved in ether. A yellow precipitate was obtained (product 1, amorphous sulfur). The breakdown products, dissolved in ether, were separated and isolated using tlc (Table I).

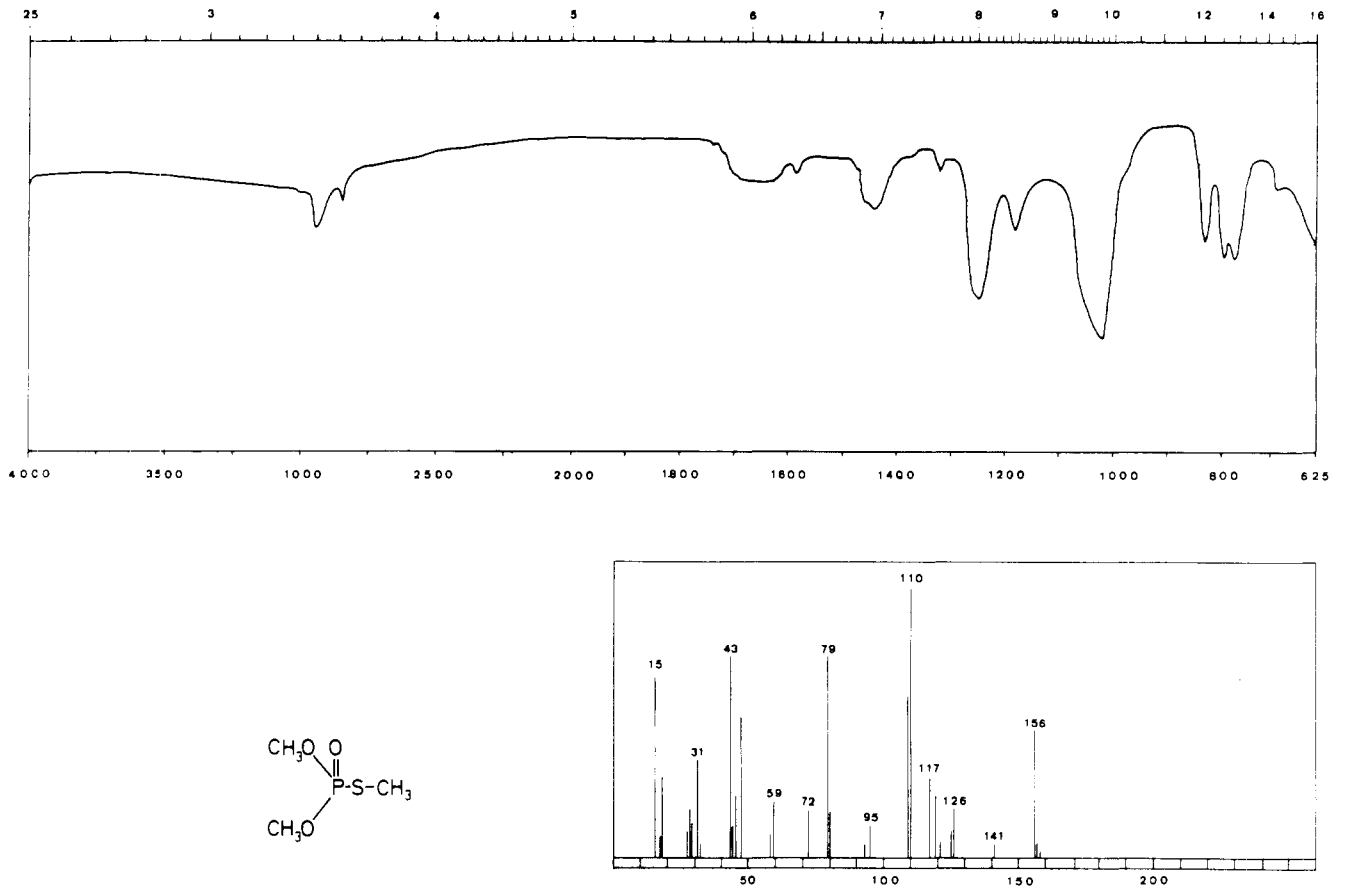


Figure 4. Infrared and mass spectra of *O,O,S*-trimethylthiophosphonic acid (product 7).

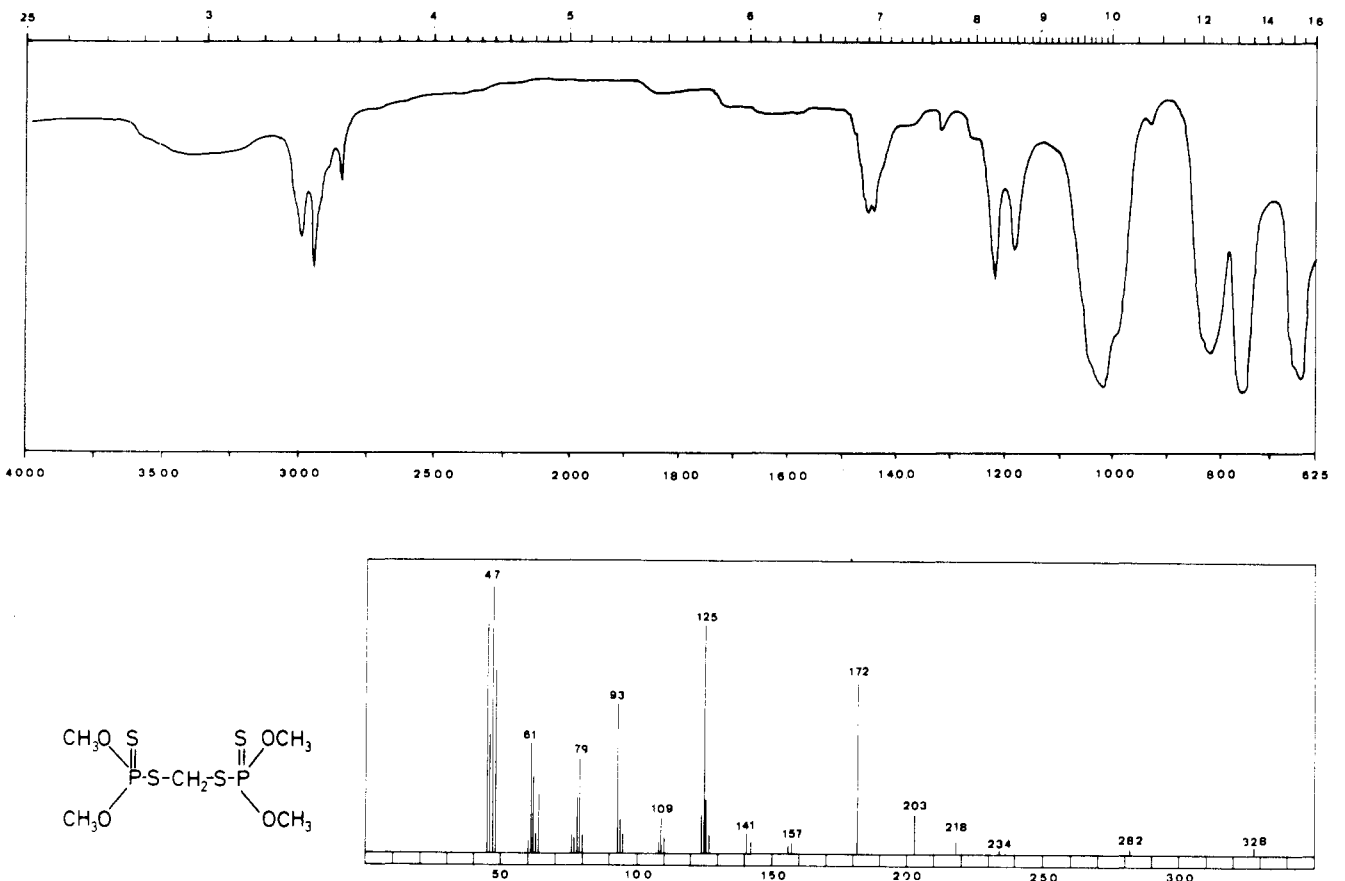


Figure 5. Infrared and mass spectra of *O,O,O',O'*-tetramethyl-*S,S*-methylbis(dithiophosphonic) acid (product 4).

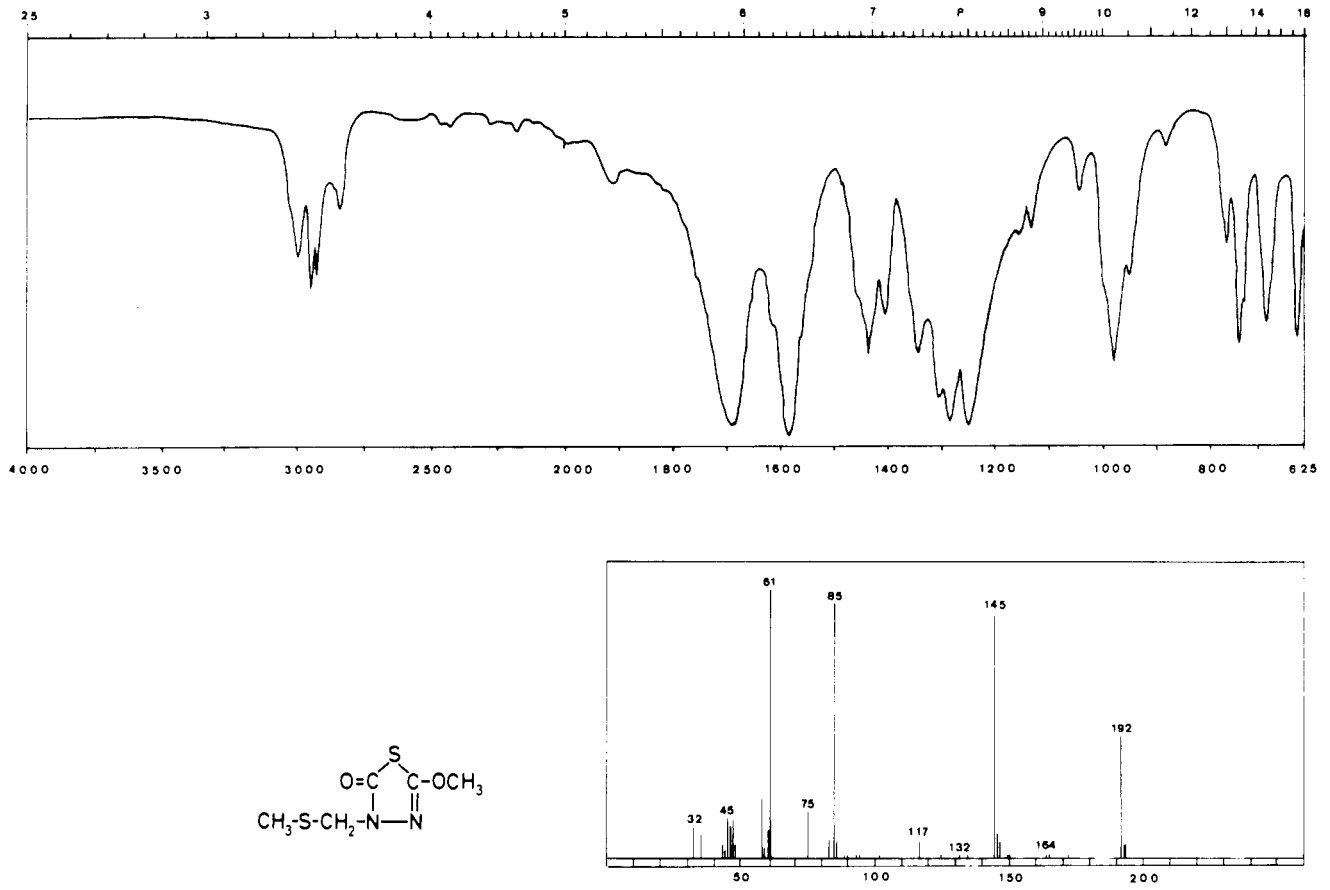


Figure 6. Infrared and mass spectra of 2-methoxy-4-methylthiomethyl- Δ^2 -1,3,4-thiadiazolin-5-one (product 3).

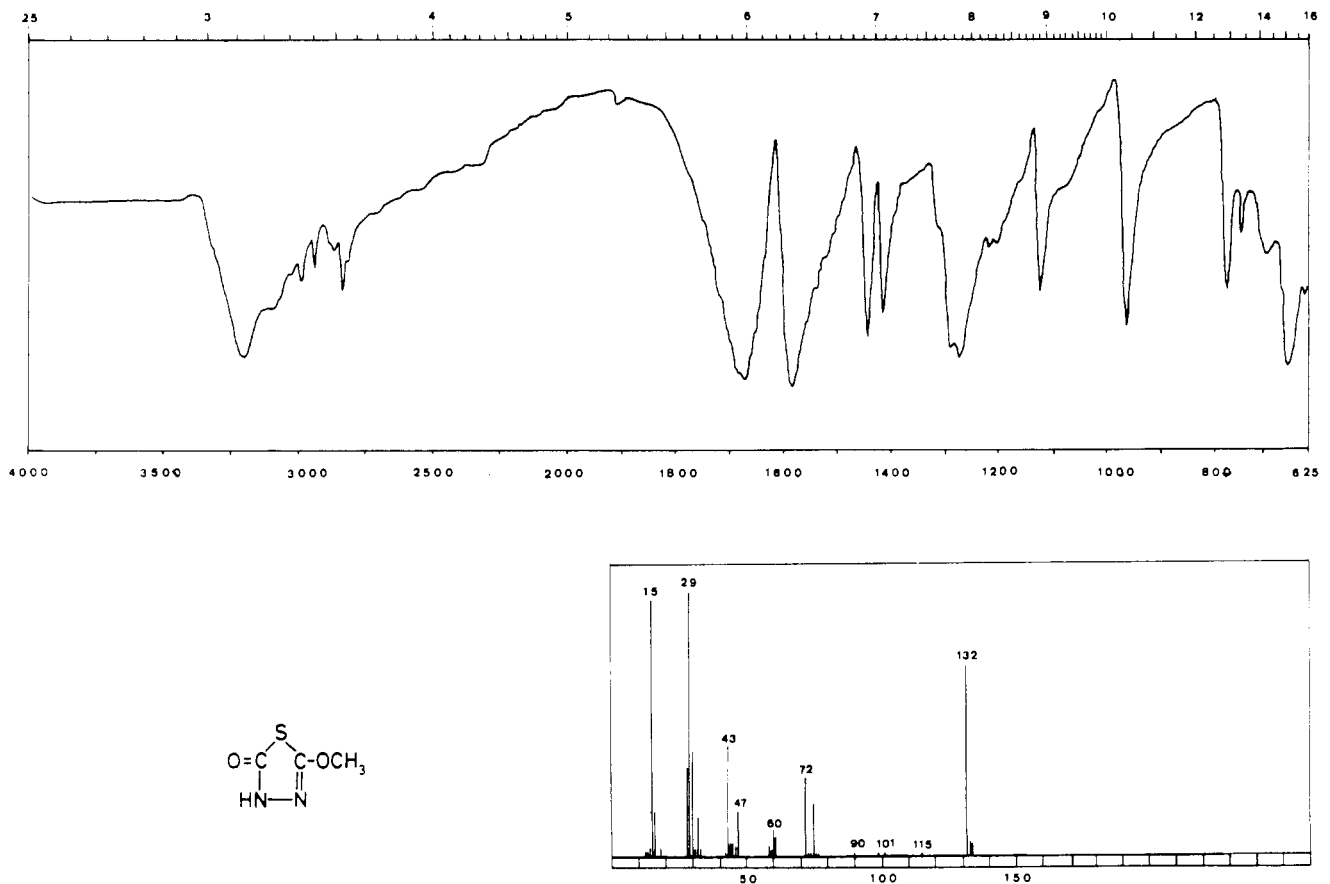


Figure 7. Infrared and mass spectra of 2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-one (product 9).

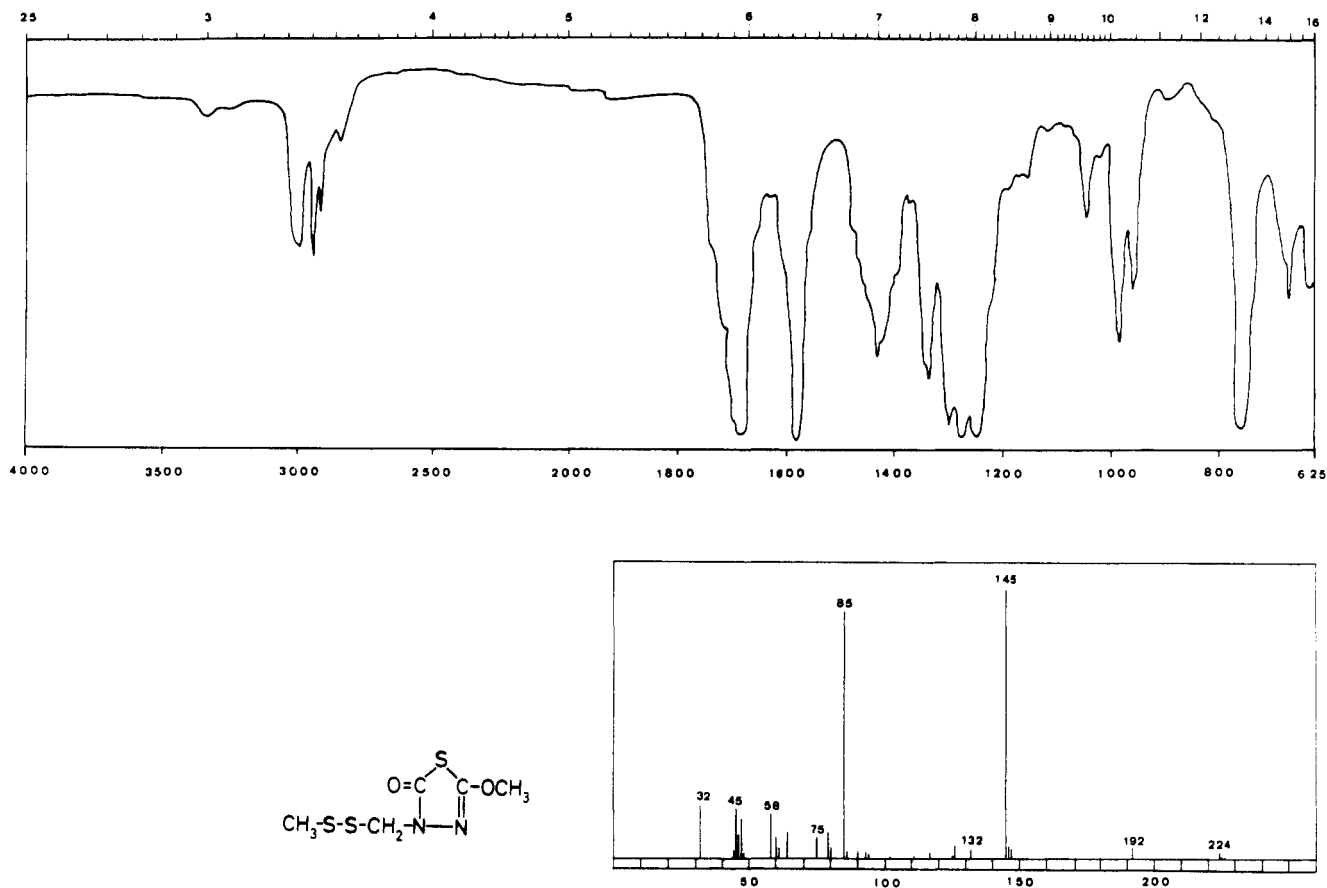


Figure 8. Infrared and mass spectra of 2-methoxy-4-methyldithiomethyl- Δ^2 -1,3,4-thiadiazolin-5-one (product 5).

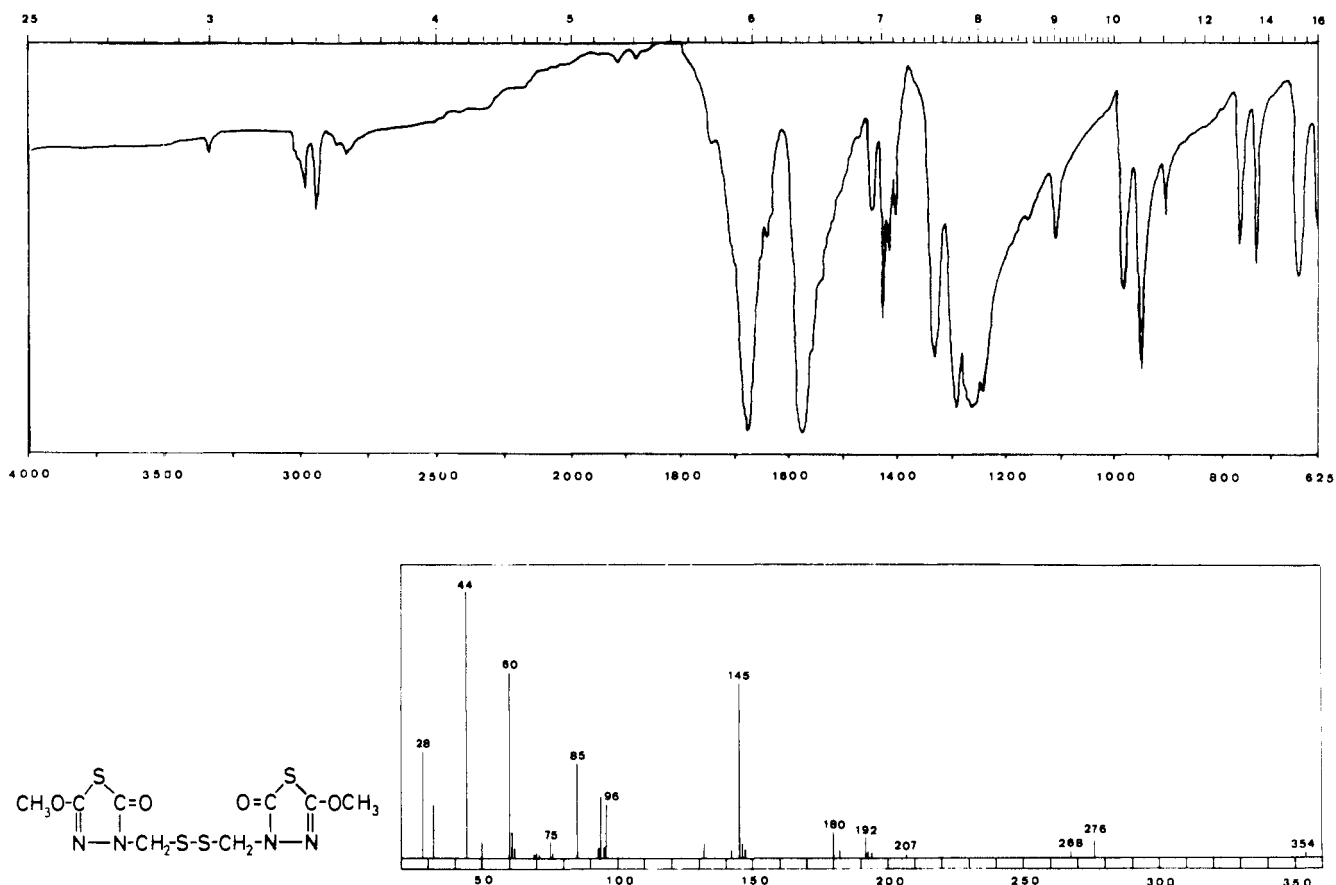


Figure 9. Infrared and mass spectra of bis(2-methoxy- Δ^2 -1,3,4-thiadiazolin-5-on-4-yl) disulfide (product 6).

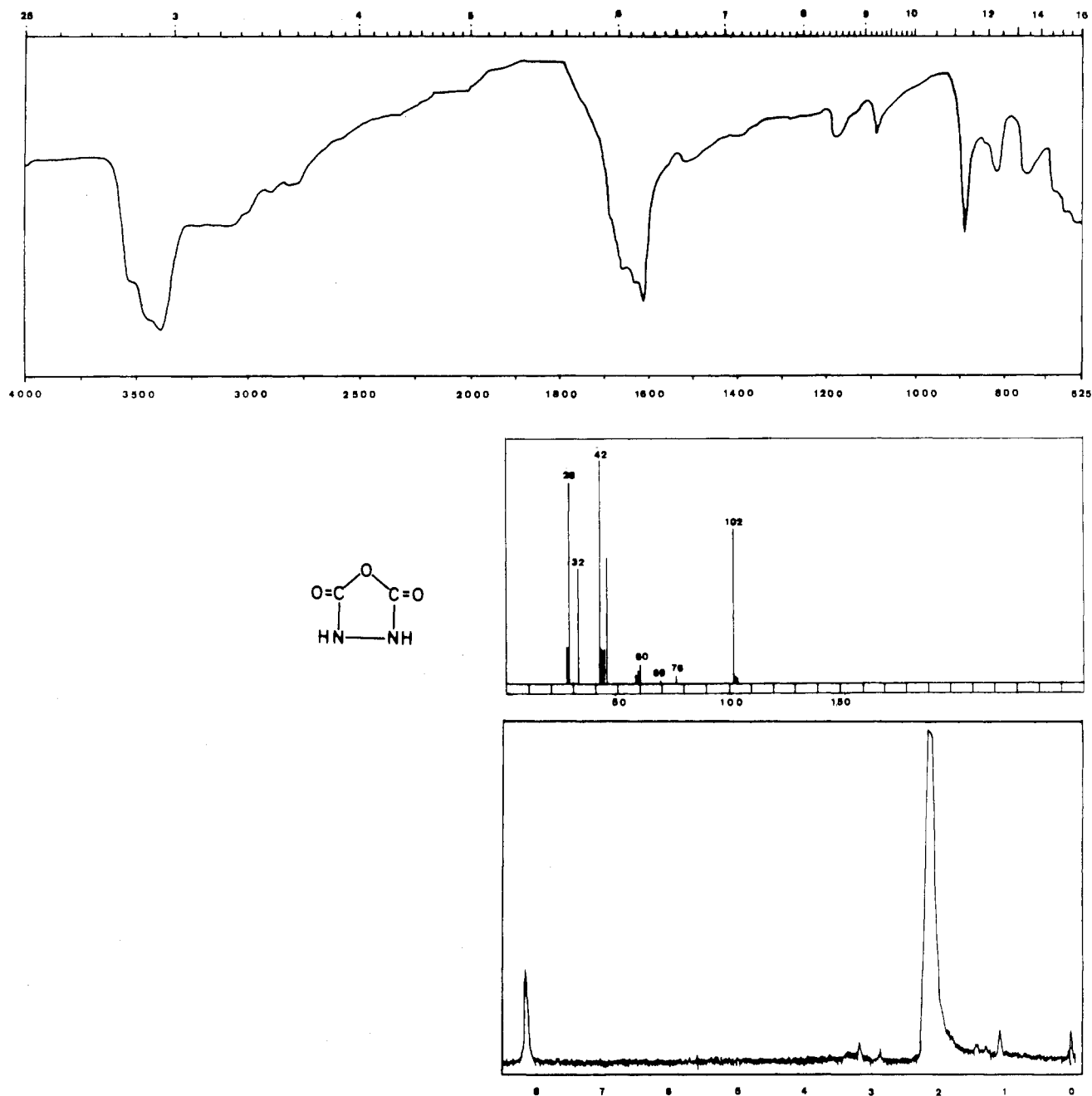


Figure 10. Infrared, mass, and nmr spectra of 1,3,4-oxodiazolidine-2,5-dione (product 10).

Chromatography on a silica gel column of the ether phase made it possible to obtain three fractions, containing, respectively, compound 2 and methidathion, compounds 3, 4, and 5, and finally compounds 6, 7, and 8. From these fractions the compounds were isolated using tlc.

The water phase was extracted with ether and the extract dried over anhydrous Na_2SO_4 and evaporated to dryness resulting in a crystalline residue containing compounds 9 and 10.

RESULTS AND DISCUSSION

Irradiating methidathion with light of different wavelengths results in a breakdown of the compound, the speed of which depends mainly on the wavelength and irradiation intensity. Glc determination of the unaltered methidathion showed that 50% was broken down after 20 hr using the 254-m μ Westinghouse lamp, after 72 hr using the 254-m μ Desaga lamp, and after 200 hr with the 365-

m μ Desaga lamp. Irradiation with the Xenon lamp resulted in a 10% breakdown after 92 hr which was also obtained after 60 hr of sunlight (or 200 hr of normal day and night exposure). Using tlc techniques a number of breakdown products were isolated and their structures determined.

Structure determination was based on the ir, mass and in some cases nmr spectra of the compounds, melting point, and all relevant information obtained by tlc, starting from the ir and mass spectra of methidathion. The interpretation of the various bands and peaks from the spectra led to the elucidation of the structure of the unknown breakdown products obtained. The ir and mass spectra are given in Figures 1-10.

Table II shows the interpretation of the different relevant bands in the ir spectra. Table III gives a survey of the peaks from the mass spectra.

Product 1, isolated as a yellow precipitate, produced no bands in the ir spectrum. The melting point (119-120°), the solubility in different solvents, and the tlc R_f values

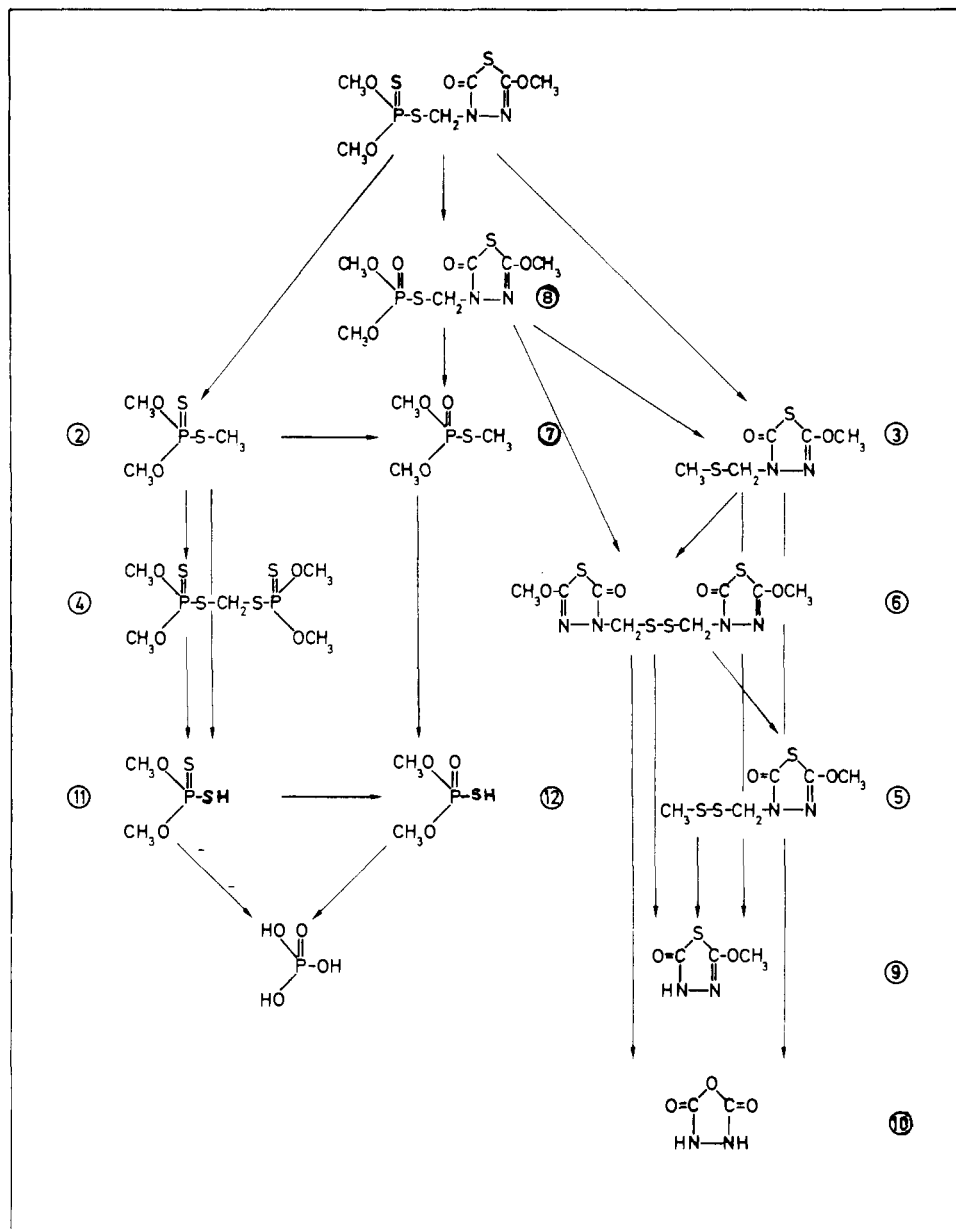


Figure 11. Proposed photochemical breakdown scheme of methidathion.

correspond with those of amorphous sulfur.

The ir spectrum of compound 8 is very similar to that of methidathion. The disappearance of the bands at 820 and 650 cm^{-1} and an increased absorption at 1250 cm^{-1} indicate the substitution of $\text{P}=\text{S}$ by $\text{P}=\text{O}$. Also, the mass spectrum with M^+ m/e 256 and the peak at m/e 156, replacing that at m/e 172, supports the proposed structure. The structure was finally confirmed through synthesis of the reference compound.

The ir spectrum of compound 2 indicates a phosphorus-containing group without the thiadiazolinone ring. The compound contains the $\text{P}=\text{S}$ group. The mass spectrum shows an intense peak of the molecular ion (m^+) at 172 and other peaks indicating the presence of a P group linked to SCH_3 groups. The peaks in the nmr spectrum are doublets due to spin coupling with the phosphorus atom. The proposed structure was confirmed by synthesis.

The ir spectrum of compound 9 indicates the presence of a thiadiazolinone ring with NH (3200 cm^{-1}) and without P. The mass spectrum shows a molecular ion at m/e 132 and a number of peaks indicating the thiadiazolinone ring. The proposed structure was confirmed by synthesis.

The ir spectrum of compound 5 shows the peaks of a

thiadiazolinone ring without P and NH and the presence of SCH_2N . The band at 1040 cm^{-1} could be attributed to an OSO group, but the intensity is rather low. The mass is 224 and the peak at m/e 192 ($\text{M}^+ - 32$) is typical for a di- or polysulfide.

The structure of compound 6 was confirmed by synthesis. The ir spectrum shows a thiadiazolinone ring without P or NH, and the presence of an SCH_2N group. The mass spectrum has a molecular ion at m/e 354 and a number of peaks indicating a thiadiazolinone ring. The peak at m/e 276 ($354 - 78, \text{SCH}_2\text{S}$) favors the proposed structure.

The ir spectrum of compound 10 presents no bands indicating the presence of either a phosphorus containing group or a thiadiazolinone ring but bands attributed to the presence of NH (3400 cm^{-1}) and C=O groups (1655-1635 cm^{-1}), reduced by intramolecular H bands with the NH groups and by conjugation with the free electron pairs on the N atoms. The mass spectrum, showing a m/e 102 molecular ion peak, confirms the absence of a P group and a thiadiazolinone ring. The peak at m/e 102 + 2 amounts to only 2% of the m/e 102 peak, indicating the absence of sulfur in the molecule. The nmr spectrum confirms the proposed structure (NH group). Thus,

Table III. Peaks of the Mass Spectra of Methidathion and Its Breakdown Products

<i>m/e</i>	Structure
354	
328	$(\text{CH}_3\text{O})_2\text{P}(=\text{S})\text{SCH}_2\text{SP}(=\text{S})(\text{OCH}_3)_2$
302	
286	
276	$m/e\ 354 - 78 = \left[\begin{array}{c} \text{S} \cdots \text{S} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \right]^+$
256	$\left[\begin{array}{c} \text{H} \\ \\ \text{O} \\ \\ \text{P}-\text{R} \\ \\ \text{CH}_3\text{O} \end{array} \right]^+$
234	$m/e\ 328 - 94 = [\text{CH}_3\text{OP}=\text{S}]$
224	
218	$m/e\ 328 - 110 = [\text{CH}_3\text{OP}(=\text{S})=\text{O}]$
203	$m/e\ 328 - 125 = [\text{CH}_3\text{O}_2\text{P}^+\text{S}]$
192	
172	$[(\text{CH}_3\text{O})_2\text{P}(=\text{S})\text{SCH}_2]^+$
157	$[(\text{CH}_3\text{O})_2\text{P}(=\text{S})\text{SH}]^+$ or $[\text{HOP}(=\text{S})\text{OCH}_2\text{SCH}_2]^+$
156	$(\text{CH}_3\text{O})_2\text{P}(=\text{O})\text{SCH}_2$
145	
141	$[(\text{CH}_3\text{O})_2\text{P}(=\text{O})\text{SH}]^+$ or $[\text{HOP}(=\text{O})\text{OCH}_2\text{SCH}_2]^+$
132	
126	$[(\text{CH}_3\text{O})_2\text{P}(=\text{S}^+)\text{H}]$
125	$(\text{CH}_3\text{O})_2\text{P}^+=\text{S}$
110	$[\text{CH}_3\text{OP}(=\text{S})(=\text{O})]^+$
109	$\text{CH}_2=\text{O}^+\text{P}(=\text{S})=\text{O}$
102	
93	$\text{CH}_2=\text{O}^+\text{P}=\text{S}$
85	$\text{CH}_2=\text{NN}=\text{C}=\text{O}^+\text{CH}_3$
79	$(\text{SPO})^+$
75	$^+\text{NHC}(\text{O})\text{S}$
61	$\text{CH}_2\text{S}^+=\text{CH}_2$
60	$(\text{O}=\text{C}=\text{S})^+$
47	CH_2S^+
45	$\text{O}=\text{COH}$
43	$\text{O}=\text{C}=\text{NH}^+$
42	(OCN)

compound 10 is a breakdown compound of the thiadiazolinone ring. It is water soluble and melts at 97–98°. The compound was not synthesized and no mention of this compound has been found in the literature. The formation of a water-soluble methidathion metabolite resulting from ring breakage followed by rearrangement of the resulting groups has been suggested by Bull (1968) and Cassidy *et al.* (1969a,b). However, they made no attempt at elucidating its structure.

Compounds 11 and 12 could be isolated from the water fraction using diazomethane. The methylated compounds were identical with compounds 2 and 7. The actual compounds were thus dithio- or thiophosphoric acid, methylated or not. It is very probable, although not demonstrated, that this also goes for phosphonic acid.

CONCLUSIONS

Structure determination of methidathion metabolites produced by uv irradiation at 254 m μ shows that methidathion is not only broken down, but that through rearrangement of certain of the fragments produced, new compounds are synthesized. This was suggested by Bull (1968) and Cassidy *et al.* (1969a,b) on the basis of the small amount of ^{14}C obtained from [^{14}C]methidathion, labeled in the thiadiazolinone ring, applied to plants and insects. A possible degradation scheme for methidathion is shown in Figure 11.

No effort was made to quantitize the isolated compounds. The highest concentration of compounds 1, 2, 6, and 10 was observed after irradiation with 254-m μ uv light, and the same compounds were also obtained with visible light. In both cases compounds 7 and 8 were produced in smaller quantities but were always clearly detectable using the enzymatic method on tlc plates. The other compounds could only be obtained after irradiation with 254-m μ uv light for longer periods of time.

LITERATURE CITED

- Bull, D. L., *J. Agr. Food Chem.* 16, 610 (1968).
 Cassidy, J. E., Murphy, R. T., Mattson, A. M., Kahrs, R. A., *J. Agr. Food Chem.* 17, 571 (1969a).
 Cassidy, J. E., Ryskiewick, D. P., Murphy, R. T., *J. Agr. Food Chem.* 17, 559 (1969b).
 Cook, J. W., *J. Ass. Offic. Agr. Chem.* 37, 989 (1954).
 Cook, J. W., *J. Ass. Offic. Agr. Chem.* 38, 826 (1955).
 Cook, J. W., Ottes, R., *J. Ass. Offic. Agr. Chem.* 42, 211 (1959).
 Eberle, D. O., Delley, R. G., Szekely, G. G., Stambac, K. H., *J. Agr. Food Chem.* 15, 213 (1967).
 Esser, H. O., Mucke, W., Alt, K. O., *Helv. Chim. Acta* 51, 513 (1968).
 Esser, H. O., Müller, P. W., *Experientia* 22, 36 (1966).
 Hoegberg, E. I., Cassaday, J. T., *J. Amer. Chem. Soc.* 73, 557 (1951).
 Mattson, A. M., Kahrs, R. A., Murphy, R. T., *J. Agr. Food Chem.* 17, 565 (1969).
 Mitchell, L. C., *J. Ass. Offic. Agr. Chem.* 44, 643 (1961).
 Mitchell, T. H., Ruzicka, J. H., Thomson, J., Wheals, B. B., *J. Chromatogr.* 32, 17 (1968).
 Polan, C. E., Hubber, J. T., Young, R. W., Osborne, J. C., *J. Agr. Food Chem.* 17, 857 (1969).
 Rufenacht, K., *Helv. Chim. Acta* 51, 518 (1968).
 Yositaka, D., Kyoichi, H., Michiko, I., Setsuko, H., Sadakazu, S., *Acta Med. Okayama* 22, 281 (1968).

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