

# Formation of Trialkyl Phosphorothioate Esters from Organophosphorus Insecticides after Exposure to Either Ultraviolet Light or Sunlight

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Five different phosphorothioate insecticides, methyl parathion, fenthion, methidathion, azinphos-methyl, and malathion, and a phosphoramidothioate, acephate, were exposed as thin films to irradiation by sunlight and ultraviolet light. With the exception of acephate, measurable amounts of different trimethyl phosphorothioate and dithioate esters, some of them having delayed toxic activity, were formed from these insecticides as a result of irradiation. The extent of photoalteration to these low molecular weight trialkyl phosphorothioates had a strong link with the UV extinction coefficient, as well as absorption maxima of the various insecticides. On the basis of known oral toxicities of the trimethyl phosphorothioate and dithioate esters and the recommended field use rates of the test insecticides, the levels of the photoalteration products formed are not expected to pose toxic hazards to farm workers.

Previous reports from this laboratory and the Medical Research Council Toxicology Unit (Carshalton, England) have described the unusual delayed toxic properties of *O,O,S*-trimethyl phosphorothioate (1) (Mallipudi et al., 1979; Umetsu et al., 1981) and *O,S,S*-trimethyl phosphorodithioate (2) (Aldridge et al., 1979). These compounds, which have been shown to exist as minor contaminants in malathion and other organophosphorus insecticides, caused delayed death in rats following a single oral dose as low as 15 mg/kg. Moreover, 1, 2, and other related organophosphorus impurities also were found to potentiate the acute mammalian toxicity of carboxylic acid ester containing organophosphorus insecticides such as malathion and phenthoate (Pellegrini and Santi, 1972; Umetsu et al., 1977). These impurities are introduced as side products formed during the various synthetic steps leading to the technical material.

The photolytic conversion of parathion into triethyl phosphorothioate (ethyl analogue of 1) as the major product upon solution irradiation with ultraviolet light has been reported (Grunwell and Erickson, 1973). Owing to the insidious toxicological properties of 1, 2, and related sulfur-containing phosphorus esters and the possibility of their photolytic formation, a study was undertaken to determine the extent to which these materials are formed upon exposure of organophosphorus insecticides to sunlight and ultraviolet light.

## MATERIALS AND METHODS

**Chemicals.** *O,O,S*-Trimethyl phosphorothioate (1), *O,S,S*-trimethyl phosphorodithioate (2), trimethyl phosphate (3), *O,O,O*-trimethyl phosphorothioate (4), and *O,O,S*-trimethyl phosphorodithioate (5) were available from earlier studies (Umetsu et al., 1977; Toia et al., 1980). Methyl parathion (6), methyl paraoxon (7), *S*-methyl parathion (8), fenthion (9), malathion (12), malaoson (13), *S*-methyl malathion (14), acephate (15), and methamidophos (16) were also available from previous studies (Hollingworth et al., 1967; Toia et al., 1980; Ryan and Fukuto, 1985; Larson, 1975; Thompson and Fukuto, 1982). Methidathion (10) and azinphos-methyl (11) were obtained, respectively, from the Ciba-Geigy Corp., Greensboro, NC, and Mobay Chemical Corp., Kansas City, MO, as technical-grade materials. Compounds 1-16 were purified to >99% by preparative TLC (see Table I). Purities were confirmed by analytical TLC on a stationary phase

**Table I. Thin-Layer Chromatography of Methyl Parathion, Fenthion, Methidathion, Azinphos-methyl, Malathion, and Acephate with Their Potential Photoalteration Products<sup>e</sup> in Various Solvent Systems on 0.25-mm Silica Gel Plates, Showing Their  $R_f$  Values**

compd	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>d</sup>
1	0.22	0.10	0.53	0.69
2	0.26	0.10	0.57	0.75
3	0.15	0.06	0.48	0.62
4	0.27	0.09	0.11	0.03
5	0.65	0.42	0.74	0.88
6	0.55	0.33	0.68	0.81
7	0.21	0.06	0.38	0.54
8	0.27	0.06	0.55	0.71
9	0.61	0.44	0.75	0.84
10	0.53	0.27	0.69	0.81
11	0.63	0.24	0.78	0.87
12	0.56	0.31	0.73	0.84
13	0.25	0.11	0.44	0.61
14	0.31	0.13	0.53	0.66
15	0.04	0.00	0.37	0.40

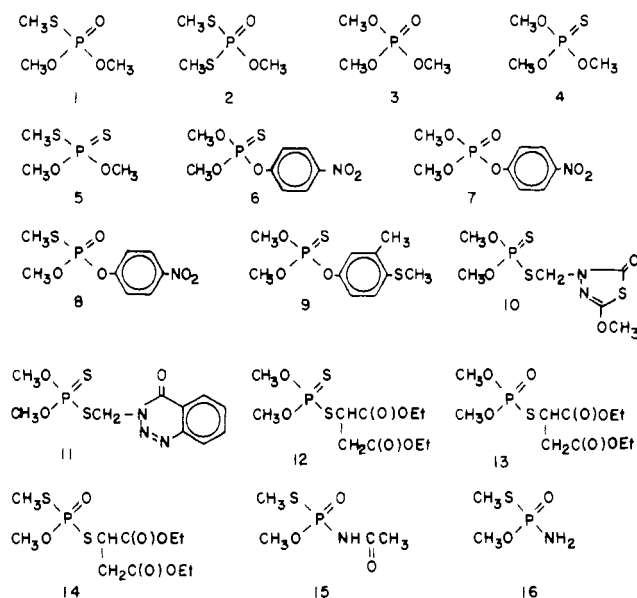
<sup>a</sup>Hexane-ethyl acetate (1:1, v/v). <sup>b</sup>Hexane-ethyl acetate (8:2, v/v). <sup>c</sup>Hexane-2-propanol (1:1, v/v). <sup>d</sup>Diethyl ether-2-propanol (8:2, v/v). <sup>e</sup>The  $R_f$  of 16 was not determined.

of silica gel and by GLC, as described under Analysis. The structures of 1-16 are given in Figure 1.

**Photolysis.** Sunlight irradiation of the various insecticides was carried out during the following periods: methyl parathion, fenthion, and methidathion in the summer of 1984; malathion and acephate in the summer of 1985; azinphos-methyl in the summer of 1986. The average maximum air temperature during these periods was 38 °C with maximum temperature ranges of 31-42, 30-44, 28-43, 30-44, 27-38, and 26-38 °C for methyl parathion, fenthion, methidathion, azinphos-methyl, malathion, and acephate, respectively. Samples of insecticide (~0.3 mmol) dissolved in benzene were deposited, in triplicate or greater, onto the bottom half of 5-cm (i.d.) Pyrex Petri dishes, and the solvent was removed under a gentle stream of nitrogen. The dishes were covered and sealed with 25- $\mu$ m-thick FEP Teflon sheets to reduce volatilization and yet allow passage of the ultraviolet component of sunlight. At different time intervals, the Petri dishes and Teflon sheets were thoroughly rinsed with ethyl acetate and after appropriate dilutions the contents were analyzed by GLC as described under Analysis.

For ultraviolet irradiation, the Teflon-covered Petri dishes were placed 1 cm below a set of five Sylvania BL-40 fluorescent lights having a maximum spectral emission at 360 nm. The temperature of the room ranged from 30 to

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**Figure 1.** Structure of the organophosphorus insecticides and potential photoalteration products.

35 °C, and the average relative humidity was 55%. Samples were processed as described above for the sunlight studies.

In both sunlight and UV irradiation, dark controls were also prepared from the test insecticide samples. They were covered with glass tops and aluminum foil and kept in the same environment as the other irradiated samples.

**Analysis.** The trimethyl phosphorus esters 1–5 were quantified by GLC on a Varian 3700 gas chromatograph equipped with a thermionic specific detector (TSD) or a Hewlett-Packard 402 gas chromatograph equipped with an alkali (KCl) flame ionization detector (AFID).

The Varian 3700 gas chromatograph was equipped with a 6 ft × 2 mm (i.d.) coiled glass column. The column packing was prepared after the surface-modified support methodology of Aue et al. (1973) utilizing 6% EGSS-X (Applied Science Laboratories, State College, PA) on HCl-extracted 80/100-mesh Chromosorb W, vacuum-coated and fluidized, conditioned for 24 h at 230 °C, and exhaustively extracted with chloroform. All the GLC packings used in this study were similarly prepared as surface-modified supports. The HP 402 gas chromatograph was equipped with a 6 ft × 2 mm (i.d.) U-shaped glass column packed with an EGSP-Z (Applied Science Laboratories) surface-modified support. Oven temperature for both the Varian 3700 and HP 402 was isothermal at 110 °C; their detector temperatures were set at 300 and 260 °C and their injection port temperatures at 250 and 230 °C, respectively. Hydrogen, air, and helium flow rates were adjusted as appropriate depending on the sensitivity desired. For the Varian 3700, quantification of products was achieved by extrapolating the experimentally determined sample peak areas to those of authentic standards on a Spectra Physics 4100 integrator. For the HP 402, quantification was achieved by relating the sample peak heights to that of a standard curve prepared with authentic standards.

The identification of compounds 1–5 was confirmed by retention index matching with authentic standards on three different columns of different polarities. The following GLC conditions were used for this purpose [instrument model, column packing stationary phase, column temperature (isothermal), detector]: (a) Varian 3700, EGSS-X, 110 °C, TSD; (b) HP 402, EGSP-Z, 110 °C, AFID; (c) Varian 1400, OV-17, 120 °C, AFID; (d) Varian

**Table II.** Detection and Quantification Limits for the Varian 3700 Gas Chromatograph Equipped with a Thermionic Detector

compd	limit of detection, <sup>a</sup> pmol	limit of quantification <sup>b</sup> (or trace limit), pmol
1	0.02	0.20
2	0.02	0.20
3	0.03	0.40
4	0.004	0.05
5	0.004	0.05
7	0.70	8.0
8	0.60	7.0
13	0.30	3.0
14	0.20	2.0
16	0.008	0.10

<sup>a</sup>The limit of detection (LOD) is the least amount of these phosphorus esters, in 3-mL total volume, that is statistically indistinguishable from an analytical blank following an injection of 3- $\mu$ L amounts into the GLC. <sup>b</sup>For this study, the limit of quantification, defined as the lowest amount of analyte at which the signal to noise ratio approaches unity, is conveniently set to be (12LOD). Detector responses below these levels are classified as trace.

1400, Carbowax 20 M terephthalic acid, 120 °C, AFID.

Methyl parathion (6), methyl paraoxon (7), *S*-methyl parathion (8), fenthion (9), acephate (15), and methamidophos (16) were analyzed by means of the HP 402 gas chromatograph equipped with AFID. The 180 cm × 2 mm (i.d.) glass column was packed with an EGSP-Z surface-modified support. Oven temperatures were set isothermally at 180 °C for 6, 9, 15, and 16 and at 170 °C for 7 and 8. Injector and detector temperatures were set at 230 and 260 °C, respectively, for the six compounds. Malathion (12), malaoxon (13), and *S*-methyl malathion (14) were analyzed on the Varian 3700 gas chromatograph equipped with a TSD. Oven temperatures were isothermally set at 200, 225, and 160 °C for 12–14, respectively. Injector and detector temperatures were fixed at 250 and 300 °C, respectively, for all three compounds. Methidathion (10) and azinphos-methyl (11) were analyzed by means of the Varian 1400 gas chromatograph equipped with AFID. For 10, the column was packed with OV-17 surface-modified support and the column oven temperature was isothermal at 200 °C. For 11, the column was packed with 6% (by wt) SE-30 on gas chrom Q (80/100 mesh) and the column temperature was isothermal at 250 °C. Injector and detector temperatures were set at 260 and 280 °C, respectively, for both compounds. In all cases, hydrogen, air, and carrier gas flow rates were set as appropriate. Quantification was carried out by extrapolating the experimentally determined sample peak heights to that of a standard curve arrived at from authentic standards. The detection and quantification limits for some of the potential photolysis products are shown in Table II.

High-pressure liquid chromatography (HPLC) was carried out with a Waters RCM-100 HPLC system equipped with a refractive index (RI) and UV detector. Owing to the poor UV absorptivities of 1–5, only the RI detector was used. The mobile phase was a mixture of pentane and ethyl acetate (8:2, v/v) isocratically delivered by a Waters 600 pump at a rate of 7 mL/min to the 8-mm-i.d. stainless steel radial pak silica gel column (Waters). Owing to the low sensitivity of the RI detector, all samples were pooled and concentrated prior to analysis.

GLC-mass spectrometry was carried out on a Hewlett-Packard 5790 gas chromatograph interfaced with a VG 7070 mass spectrometer. The 30 m × 0.25 mm (i.d.) DB-5 capillary column employed for the separations was held at 60 °C for 2 min and was then programmed at a rate of

Table III. Photoalteration of Methyl Parathion Irradiated with Sunlight and Ultraviolet Light As Determined by GLC

irrad time, h	amount of product, nmol				
	1	3	4	6	8
	Sunlight				
0.00	ND	ND	ND	$(0.41 \pm 0.02) \times 10^6$	ND
3.00	$160.0 \pm 4.0$	$45.0 \pm 2.0$	ND	$(0.32 \pm 0.02) \times 10^6$	ND
5.00	$240.0 \pm 12.0$	$61.0 \pm 4.0$	ND	$(0.29 \pm 0.04) \times 10^6$	ND
7.50	$342.0 \pm 10.0$	$71.0 \pm 4.0$	ND	$(0.32 \pm 0.01) \times 10^6$	ND
10.00	$111.0 \pm 5.0$	$71.0 \pm 4.0$	ND	$(0.33 \pm 0.01) \times 10^6$	ND
13.25	$322.0 \pm 11.0$	$80.0 \pm 4.0$	ND	$(0.33 \pm 0.01) \times 10^6$	ND
14.00	$230.0 \pm 8.0$	$65.0 \pm 5.0$	ND	$(0.28 \pm 0.02) \times 10^6$	ND
(2.58 <sup>a</sup> )	(19.6 <sup>a</sup> )	ND	(4.4 <sup>a</sup> )	(21.63 <sup>a</sup> )	ND
	UV Light				
0.00	ND	ND	ND	$(0.30 \pm 0.03) \times 10^6$	ND
5.00	$299.4 \pm 7.4$	ND	ND	$(0.31 \pm 0.03) \times 10^6$	$1037.2 \pm 19.0$
16.00	$2516.0 \pm 23.0$	$142.9 \pm 7.1$	ND	$(0.27 \pm 0.03) \times 10^6$	ND
22.00	$2852.6 \pm 7.4$	$528.6 \pm 2.1$	ND	$(0.22 \pm 0.05) \times 10^6$	$316.5 \pm 15.5$
28.00	$4262.8 \pm 5.8$	$285.7 \pm 14.2$	ND	$(0.24 \pm 0.04) \times 10^6$	ND
41.00	$4487.2 \pm 2.0$	$1035.7 \pm 5.0$	ND	$(0.27 \pm 0.01) \times 10^6$	ND
46.00	$4631.4 \pm 1.6$	$1642.9 \pm 7.9$	ND	$(0.23 \pm 0.04) \times 10^6$	ND
48.00	$1602.6 \pm 2.4$	$1196.4 \pm 3.2$	ND	$(0.21 \pm 0.02) \times 10^6$	$507.6 \pm 8.3$
72.00	$1487.2 \pm 3.7$	$928.6 \pm 6.3$	ND	$(0.24 \pm 0.05) \times 10^6$	$626.1 \pm 9.2$

<sup>a</sup> These values were obtained only in one sunlight exposure study.

Table IV. Photoalteration of Methyl Parathion by Sunlight and Ultraviolet Light: Product Analysis by GC-MS

spectral data	tentative identification
156 (M <sup>+</sup> , 57%), 141 (7), 126 (16), 125 (10), 111 (5), 110 (100), 109 (62), 95 (10), 80 (15), 79 (46)	(MeO) <sub>2</sub> P(O)SMe
218 (M <sup>+</sup> , 100%), 167 (28), 149 (50), 125 (38), 109 (88), 91 (52)	(MeO) <sub>2</sub> P(O)P(O)(OMe)
234 (M <sup>+</sup> , 55%), 204 (100), 189 (11), 173 (76), 149 (36), 126 (67), 109 (38), 79 (16)	(MeO) <sub>2</sub> P(O)OP(O)(OMe) <sub>2</sub>
220 (M <sup>+</sup> ) several types	unknown
140 (M <sup>+</sup> , 15%), 111 (2), 110 (100), 109 (10), 95 (15), 79 (21), 78 (7)	(MeO) <sub>3</sub> P=O
167 (M <sup>+</sup> )	unknown
243 (M <sup>+</sup> )	unknown
247 (M <sup>+</sup> , 6%), 125 (76), 109 (100), 93 (15), 79 (17)	(MeO) <sub>2</sub> P(O)OAr- <i>p</i> -NO <sub>2</sub>

8 °C/min to 250 °C when the temperature was held for 40 min. Sample injections were carried out in a splitless mode and the injection port, ion source, and detector temperatures were 180, 200, and 200 °C, respectively. An electron energy of 20 eV was used for sample bombardment in the VG 7070 and the mass range 33–500 amu was

scanned every 1 s at a resolution of 1000.

## RESULTS

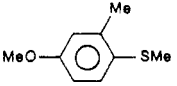
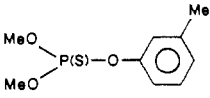
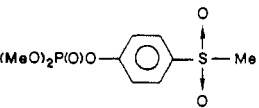
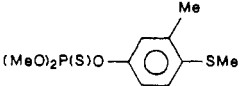
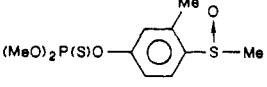
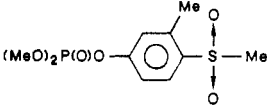
**Photolysis of Methyl Parathion.** GLC analysis of products obtained following exposure of methyl parathion (6) to sunlight indicated the formation of *O,O,S*-trimethyl phosphorothioate (1) and trimethyl phosphite (3) as the principal trimethyl phosphorus esters (Table III). A trace of *O,O,O*-trimethyl phosphorothioate (4) was detected in a single experiment, but subsequent attempts to repeat its detection were not successful. Compounds 1 and 3 reached their maximum levels at 7.5 and 13.25 h, respectively, forming 0.08% and 0.02% of the initial methyl parathion exposed to sunlight. The amount of methyl parathion dropped to 70% of its original value at the end of the 14-h sun irradiation period.

Irradiation of methyl parathion with ultraviolet light resulted in substantially larger amounts of 1 and 3 and additionally yielded small amounts of *O,S*-dimethyl *O-p*-nitrophenyl phosphorothioate (8), the *S*-methyl isomer of methyl parathion. Highest levels of 1 and 3 were observed after 46 h of ultraviolet irradiation, reaching 1.5% and 0.55%, respectively, of the original methyl parathion. The amount of 8 reached the maximum level of 0.35% after

Table V. Photoalteration of Fenthion Irradiated with Sunlight and Ultraviolet Light: Product Analysis

irrad time, h	amount of product, nmol			
	1	3	5	9
	Sunlight			
0.00	ND	ND	ND	$(0.31 \pm 0.007) \times 10^6$
4.00	$8.3 \pm 0.01$	$20.0 \pm 0.10$	ND	$(0.30 \pm 0.02) \times 10^6$
7.00	$33.0 \pm 0.01$	$90.0 \pm 0.08$	ND	$(0.30 \pm 0.01) \times 10^6$
9.50	$6.3 \pm 0.02$	$10.0 \pm 0.04$	ND	$(0.20 \pm 0.08) \times 10^6$
11.00	$26.0 \pm 0.50$	$40.0 \pm 0.20$	ND	$(0.20 \pm 0.04) \times 10^6$
12.50	$73.0 \pm 0.80$	$40.0 \pm 0.50$	ND	$(0.20 \pm 0.002) \times 10^6$
14.50	$80.0 \pm 0.70$	$70.0 \pm 0.50$	ND	$(0.13 \pm 0.01) \times 10^6$
17.50	$110.0 \pm 0.90$	$40.0 \pm 0.40$	ND	$(0.20 \pm 0.003) \times 10^6$
	UV Light			
0.00	ND	ND	ND	$(0.26 \pm 0.01) \times 10^6$
5.00	$101.1 \pm 4.8$	ND	$4.8 \pm 0.01$	$(0.27 \pm 0.03) \times 10^6$
16.00	$114.4 \pm 20.0$	ND	$6.4 \pm 1.4$	$(0.26 \pm 0.03) \times 10^6$
22.00	$101.6 \pm 12.0$	ND	$3.8 \pm 0.2$	$(0.28 \pm 0.01) \times 10^6$
28.00	$150.9 \pm 2.8$	ND	$3.6 \pm 0.05$	$(0.27 \pm 0.02) \times 10^6$
41.00	$102.5 \pm 2.5$	ND	$3.5 \pm 0.05$	$(0.25 \pm 0.01) \times 10^6$
46.00	$146.3 \pm 11.0$	ND	$3.5 \pm 0.06$	$(0.22 \pm 0.02) \times 10^6$
48.00	$76.2 \pm 5.7$	ND	$3.2 \pm 0.06$	$(0.21 \pm 0.02) \times 10^6$
72.00	$393.4 \pm 50.0$	ND	$3.0 \pm 0.1$	$(0.22 \pm 0.03) \times 10^6$

**Table VI. Photoalteration of Fenthion by Sunlight and Ultraviolet Light: Product Analysis by GC-MS**

spectral data	tentative identification
168 (M <sup>+</sup> , 100%), 153 (52), 138 (19), 109 (11), 45 (11)	
232 (M <sup>+</sup> , 100%), 200 (8), 169 (9), 125 (23), 109 (48), 93 (13), 79 (9)	
167 (M <sup>+</sup> ) 220 (M <sup>+</sup> ), several types	unknown unknown
266 (M <sup>+</sup> , 66%), 135 (100), 109 (66), 93 (10), 71 (11), 57 (16), 43 (14)	
278 (M <sup>+</sup> , 100%), 263 (8), 184 (16), 153 (24), 125 (48)	
294 (M <sup>+</sup> , 100%), 278 (55), 216 (25), 184 (14), 169 (52), 141 (51), 125 (60), 109 (14), 84 (9), 70 (12), 57 (15)	
294 (M <sup>+</sup> , 64%), 279 (100), 247 (7), 169 (33), 153 (23), 138 (24), 125 (84), 109 (46), 93 (21), 79 (12), 43 (8)	

irradiation for 5 h. The formation of 1 and 8 as photolysis products of methyl parathion was also verified by HPLC. Some products from the five other irradiation experiments were also confirmed by HPLC.

In all cases of methyl parathion irradiation with either sun or ultraviolet light, a viscous, charcoallike substance was formed that was virtually insoluble in ethyl acetate, acetone, or benzene. This substance appeared to be similar in nature to the black, polymeric material previously reported to be formed from the thermal decomposition of methyl parathion (McPherson and Johnson, 1956). However, since these visual changes were not observed in the dark control samples, it would be inappropriate to regard them as attributable to purely thermal effects only.

GC-MS analysis of the mixture obtained from the pooled samples following sunlight exposure of methyl parathion showed the presence of at least 11 different compounds. Mass spectral fragmentation patterns indicated the presence of methyl paraoxon (7), tetramethyl

pyrophosphate, and different substituted phenols of unknown structures, as well as 1 and 3. GC-MS analysis of the pooled samples from ultraviolet light exposure indicated similar products although the GC signal intensities were generally higher than those from sunlight photolysis. However, tetramethyl diphosphate, a compound not observed among the sunlight products, was indicated by its MS fragmentation pattern. Compounds tentatively identified by GC-MS and their MS fragmentation data are given in Table IV.

**Photolysis of Fenthion.** As was observed with methyl parathion, irradiation of fenthion (9) with sunlight yielded the same two trialkyl phosphorus esters (1 and 3) as major products (Table V). Compound 3 reached its peak value after 7-h irradiation, forming 0.03% of the initially irradiated fenthion. The delayed toxic product 1 increased gradually, attaining a maximum value of 0.04% after 17.5 h of sunlight exposure. The level of fenthion dropped to 65% of its initial amount over the 17.5-h exposure period.

A change in the spectrum of compounds formed following irradiation of fenthion with ultraviolet light was observed. As in the case of methyl parathion, compound 1 was the major trimethyl phosphorus ester observed, reaching a maximum value of 0.15% of the initial fenthion after exposure for 72 h. In contrast to sunlight irradiation of fenthion, 3 was not observed and in its place minute amounts of *O,O,S*-trimethyl phosphorodithioate (5) were detected, the highest amount consisting of a mere 0.003% of the original fenthion after 16-h exposure. Over the 72-h ultraviolet irradiation time span, 85% of the initially exposed fenthion was recovered as fenthion.

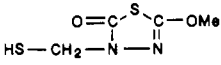
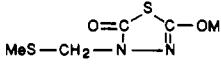
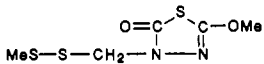
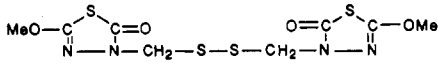
In the irradiation studies with either ultraviolet or sunlight, other alteration products were also observed as peaks in the GLC trace. However, owing to the limited availability of authentic standards none of these were identified. Further, none of these unknowns had GLC retention times that matched those of the trimethyl phosphorus esters, i.e., 1-5. GC-MS analysis of the sunlight-irradiated fenthion showed at least 12 different compounds in addition to 1 and 5. The same range of products was also observed for ultraviolet light photolysis of fenthion, although the levels here were many orders of magnitude higher than the sun-irradiated samples. Compounds tentatively identified on the basis of their MS fragmentation patterns are indicated in Table VI, along with the MS data.

**Photolysis of Methidathion.** GLC analysis showed the presence of 1, 2, and 5 upon exposure of methidathion, a phosphorodithioate insecticide, to sunlight. Of these, 2

**Table VII. Photoalteration of Methidathion Irradiated with Sunlight and Ultraviolet Light: Product Analysis**

irrad time, h	amount of product, nmol			methidathion
	1	2	5	
	Sunlight			
0.00	ND	ND	ND	(27.0 ± 0.01) × 10 <sup>4</sup>
2.75	4.02 ± 0.002	ND	5.67 ± 0.006	(26.0 ± 0.2) × 10 <sup>4</sup>
3.50	4.72 ± 0.004	tr	6.76 ± 0.007	(25.0 ± 0.4) × 10 <sup>4</sup>
5.00	4.37 ± 0.003	tr	5.08 ± 0.005	(23.0 ± 0.8) × 10 <sup>4</sup>
6.00	4.85 ± 0.003	22.74 ± 0.80	5.73 ± 0.01	(22.0 ± 0.4) × 10 <sup>4</sup>
7.00	9.80 ± 0.008	22.90 ± 0.60	6.85 ± 0.04	(19.0 ± 0.5) × 10 <sup>4</sup>
	Ultraviolet Light			
0.00	ND	ND	ND	(21.0 ± 0.3) × 10 <sup>4</sup>
5.00	tr	129.84 ± 3.0	38.89 ± 0.06	(21.0 ± 0.3) × 10 <sup>4</sup>
16.00	tr	171.02 ± 2.5	38.95 ± 0.08	(21.0 ± 0.5) × 10 <sup>4</sup>
22.00	tr	151.47 ± 4.7	41.13 ± 0.02	(32.0 ± 0.2) × 10 <sup>4</sup>
28.00	tr	169.64 ± 3.8	44.06 ± 0.02	(25.0 ± 0.6) × 10 <sup>4</sup>
41.00	tr	189.75 ± 7.0	54.29 ± 0.09	(25.0 ± 0.7) × 10 <sup>4</sup>
46.00	tr	238.42 ± 8.6	62.33 ± 0.05	(19.0 ± 0.6) × 10 <sup>4</sup>
48.00	tr	263.11 ± 4.0	71.51 ± 0.01	(22.0 ± 0.4) × 10 <sup>4</sup>
72.00	tr	160.61 ± 3.6	73.51 ± 0.04	(15.0 ± 0.9) × 10 <sup>4</sup>

**Table VIII. Photoalteration of Methidathion by Sunlight and Ultraviolet Light: Product Analysis by GC-MS**

spectral data	tentative identification
172 (M <sup>+</sup> , 100%), 142 (8), 125 (67), 109 (19), 93 (72), 79 (17), 63 (10), 47 (10)	(MeO) <sub>2</sub> P(S)SMe
178 (M <sup>+</sup> , 25%), 145 (100), 132 (56), 85 (66), 75 (21), 58 (21), 45 (33)	
192 (M <sup>+</sup> , 48%), 145 (100%), 85 (75), 75 (10), 61 (62), 47 (8)	
220 (M <sup>+</sup> ), several types	unknown
224 (M <sup>+</sup> , <2%), 145 (100), 121 (10), 85 (94), 58 (21), 45 (8)	
354 (M <sup>+</sup> , <2%), 276 (18), 192 (9), 172 (32), 145 (100), 125 (21), 93 (23), 85 (97), 75 (8), 61 (16), 47 (13)	
204 (M <sup>+</sup> , 75%), 172 (7), 157 (100), 145 (9), 125 (45), 111 (16), 94 (15), 79 (16), 63 (51), 47 (11)	(MeS) <sub>3</sub> P=S

was found in the largest proportion after 7 h, comprising only 0.0085% of the originally applied methidathion. After the 7-h irradiation period, 72% of the applied methidathion still remained on the petri dishes.

Upon exposure to UV irradiation, the product profiles were still the same but 2 and 5 were formed in substantially larger quantities while 1 was present only in trace amounts. The proportion of 2 and 5 attained their highest levels at 48 and 72 h, respectively, comprising 0.035% and 0.013% of the originally applied methidathion. Over the 72-h span of this irradiation study, the levels of methidathion left on the Petri dishes dropped to 71% of its original value.

These results are shown in Table VII.

GC-MS analysis of the mixture obtained by pooling all the irradiated samples confirmed the presence of 2 and 5. It also indicated the presence of *S,S,S*-trimethyl phosphorotetrathioate, 2-methoxy-4-[(methylthio)methyl]-Δ<sup>2</sup>-1,3,4-thiadiazolin-5-one, 2-methoxy-4-(thiomethyl)-Δ<sup>2</sup>-1,3,4-thiadiazolin-5-one, 2-methoxy-4-[(methylthio)methyl]-Δ<sup>2</sup>-1,3,4-thiadiazolin-5-one, bis(2-methoxy-5-oxo-Δ<sup>2</sup>-1,3,4-thiadiazolin-4-yl) disulfide and a series of substituted phenols. As with GLC, the product profiles for UV- and sunlight-mediated photolysis were the same, except for the higher concentrations found in the former. The spectra of these tentatively identified irradiation products are shown in Table VIII.

**Photolysis of Azinphos-methyl.** The product profiles obtained upon irradiation of azinphos-methyl, also a phosphorodithioate insecticide, with sunlight and ultraviolet light were largely similar to those of methidathion (Table IX). Under sunlight irradiation, 1, 2, and 5 were formed, with 2 being present in the highest amounts. At its maximum level following 25 h of irradiation, it comprised only 0.003% of the original starting material. The amounts of 1 and 5 were even smaller, comprising 0.001% and 0.002%, respectively, at their highest values, 21 h after irradiation. After 25 h of irradiation, the level of azinphos-methyl dropped to 63% of its initial amount.

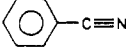
Irradiation with ultraviolet light yielded the same spectrum of products, albeit in much higher levels. However, as against sunlight irradiation, 5 was the highest of the delayed toxic photolysis products formed, comprising 0.02% of the original azinphos-methyl at its highest level, 72 h of irradiation. Compounds 1 and 2 were at their highest levels at 28 h of irradiation, comprising, respectively, 0.002% and 0.009% of the original starting material. Over the 72-h irradiation span, the amount of azinphos-methyl remaining in the Petri dishes comprised 69% of the initial levels.

GC-MS analysis of the pooled irradiated samples confirmed the presence of 1 and 5. In addition, it also indicated the presence of at least 12 other compounds including benzonitrile, *O,O*-dimethyl phosphorodithioic acid, and *O,O,O',O'*-tetramethyl *S,S'*-methylene diphosphorodithioate (Table X). The trend observed with methyl parathion also continued here, with UV-derived photolysis products being found in higher yields than those from sunlight.

**Table IX. Photoalteration of Azinphos-methyl Irradiated with Sunlight and Ultraviolet Light: Product Analysis**

irrad time, h	amount of product, nmol			
	1	2	5	azinphos-methyl
	Sunlight			
0.00	ND	ND	ND	(27.0 ± 0.8) × 10 <sup>4</sup>
2.00	tr	tr	tr	(27.0 ± 1.4) × 10 <sup>4</sup>
4.00	tr	tr	tr	(25.0 ± 1.3) × 10 <sup>4</sup>
6.00	tr	tr	tr	(24.0 ± 0.6) × 10 <sup>4</sup>
8.00	tr	tr	3.40 ± 2.40	(17.0 ± 1.1) × 10 <sup>4</sup>
12.00	tr	3.65 ± 0.63	3.80 ± 1.60	(13.0 ± 2.4) × 10 <sup>4</sup>
16.50	tr	5.04 ± 1.20	2.90 ± 0.72	(15.0 ± 1.0) × 10 <sup>4</sup>
21.00	3.10 ± 1.80	4.85 ± 1.72	4.60 ± 2.10	(16.0 ± 2.1) × 10 <sup>4</sup>
25.00	tr	8.70 ± 1.90	4.30 ± 1.30	(17.0 ± 3.2) × 10 <sup>4</sup>
	Ultraviolet Light			
0.00	ND	ND	ND	(26.0 ± 0.2) × 10 <sup>4</sup>
5.00	tr	12.83 ± 0.50	tr	(25.0 ± 1.1) × 10 <sup>4</sup>
16.00	tr	16.01 ± 3.50	tr	(26.0 ± 0.5) × 10 <sup>4</sup>
22.00	4.30 ± 0.50	16.83 ± 2.90	6.30 ± 0.45	(23.0 ± 1.4) × 10 <sup>4</sup>
28.00	4.70 ± 3.10	22.28 ± 4.50	15.60 ± 0.10	(23.0 ± 1.3) × 10 <sup>4</sup>
41.00	2.50 ± 1.00	12.14 ± 0.003	25.00 ± 0.20	(21.0 ± 1.6) × 10 <sup>4</sup>
46.00	1.80 ± 0.30	12.35 ± 0.20	27.69 ± 1.20	(20.0 ± 1.8) × 10 <sup>4</sup>
48.00	1.30 ± 1.10	13.25 ± 0.04	37.62 ± 0.80	(19.0 ± 2.1) × 10 <sup>4</sup>
72.00	1.70 ± 1.20	15.35 ± 0.20	58.60 ± 0.40	(18.0 ± 2.2) × 10 <sup>4</sup>

**Table X. Photoalteration of Azinphos-methyl by Sunlight and Ultraviolet Light: Product Analysis by GC-MS**

spectral data	tentative identification
104 (M + 1, 84%), 103 (M <sup>+</sup> , 100%), 77 (6), 76 (34), 75 (9), 74 (4), 63 (3), 52 (5), 51 (9), 50 (16), 49 (3)	
160 (M + 2, 6%), 159 (M + 1, 3%), 158 (M <sup>+</sup> , 66%), 128 (9), 127 (11), 126 (13), 125 (100), 124 (66), 96 (7), 95 (28), 94 (4), 93 (21), 80 (9), 79 (31), 78 (69), 77 (6), 64 (15), 63 (34), 62 (9), 60 (19), 59 (12), 47 (42), 46 (28), 45 (67)	(MeO) <sub>2</sub> P(S)SH
158 (M + 2, 5%), 157 (M + 1, 2%), 156 (M <sup>+</sup> , 46%), 141 (8), 126 (17), 125 (17), 110 (100), 109 (69), 95 (15), 80 (19), 79 (78), 61 (9), 47 (42), 46 (16), 45 (28)	(MeO) <sub>2</sub> P(O)SMe
174 (M + 2, 9%), 173 (M + 1, 5%), 172 (M <sup>+</sup> , 100%), 126 (24), 125 (80), 109 (26), 94 (12), 93 (97), 79 (38), 64 (11), 63 (32), 62 (11), 47 (48), 45 (25)	(MeO) <sub>2</sub> P(S)SMe
154 (M <sup>+</sup> , 11%), 106 (36), 93 (8), 61 (100), 60 (6), 47 (9), 46 (16), 45 (40)	HC(SMe) <sub>3</sub>
206 (M + 2, 3%), 204 (M <sup>+</sup> , 22%), 125 (100), 105 (6), 93 (27), 79 (27), 63 (11), 47 (18), 45 (11)	(MeO) <sub>2</sub> P(S)SSMe
204 (3%), 172 (3), 158 (3), 151 (5), 150 (11), 149 (100), 134 (27), 125 (17), 119 (19), 116 (35), 104 (13), 103 (16), 91 (23), 90 (15), 76 (11), 75 (13), 64 (14), 63 (19), 51 (12), 47 (25), 46 (22), 45 (32)	unknown
222 (3%), 220 (6), 185 (12), 160 (9), 158 (93), 149 (23), 127 (7), 125 (100), 116 (20), 95 (9), 93 (54), 79 (20), 63 (20), 47 (27), 45 (19)	unknown
220 (M + 2, 3%), 218 (M <sup>+</sup> , 21%), 203 (2), 127 (3), 126 (4), 125 (15), 93 (43), 79 (7), 64 (3), 63 (9), 62 (6), 61 (100), 47 (12), 46 (9), 45 (20)	(MeO) <sub>2</sub> P(S)SCH <sub>2</sub> SMe
205 (7%), 204 (3), 203 (46), 171 (27), 157 (8), 125 (100), 93 (34), 79 (20), 63 (9), 47 (18), 46 (13), 45 (26)	unknown
197 (2%), 195 (16), 179 (8), 136 (26), 108 (11), 69 (8), 63 (10), 61 (100), 47 (5), 46 (7), 45 (21), 42 (3)	unknown
205 (7%), 204 (3), 203 (54), 157 (12), 125 (34), 106 (26), 93 (34), 79 (9), 63 (10), 61 (100), 47 (15), 46 (13), 45 (25)	unknown
261 (3%), 260 (3), 259 (25), 135 (7), 134 (12), 125 (100), 93 (68), 90 (8), 79 (16), 63 (10), 61 (3), 47 (13)	unknown

**Photolysis of Malathion.** Product analysis by GLC after sunlight irradiation indicated the formation of 1-3, 5, 13, and 14. However, 2, 5, 13, and 14 were present in only trace amounts. The levels of 1 and 3 formed were very small, reaching their maximum values at 16.5 and 25 h, respectively, when they comprised 0.01% and 0.0008% of the originally applied malathion. At the end of the 25-h irradiation time span, there was no measurable decrease in the level of the initially applied malathion on the Petri dishes. These results are shown in Table XI.

The products were largely the same when the radiant energy source was UV light. Here again, 1-3, 5, 13, and 14 were formed in detectable amounts. However, 2, 13, and 14 were again present in trace quantities. The levels of 1, 3, and 5 were very small, as in sunlight photolysis, attaining their peak values at 22, 5, and 72 h where they made up 0.008%, 0.002%, and 0.004%, respectively, of the originally deposited malathion. At the end of the 72-h irradiation period, 84% of the deposited malathion still remained on the Petri dishes.

**Photolysis of Acephate.** Neither sunlight nor UV light measurably decreased the amounts of acephate deposited on the Petri dishes even after irradiation periods of 25 and 72 h, respectively. The initial deposit of acephate was 27.0 ± 0.009 nmol, and recovered amounts ranged from 25.0 ± 0.010 to 28 ± 0.030 nmol. Besides, no potential products, including 1-5 and 16, were present at detectable levels.

#### DISCUSSION

Solution photolysis of parathion (*O,O*-diethyl *O-p*-nitrophenyl phosphorothioate) in ethanol or tetrahydrofuran is reported to result in relatively high yields (~39%) of *O,O,S*-triethyl phosphorothioate (OOS-Et), the ethyl analogue of the delayed toxic compound 1 (Grunwell and Erickson, 1973). Although OOS-Et has also been shown to have delayed toxic properties, it is somewhat less toxic than either 1 or 2, the trimethyl phosphorodithioate ester. Therefore, a study of the formation of 1 or 2 from selected dimethyl phosphorothioate and phosphorodithioate insecticides was made to determine the extent to which these delayed toxic compounds are formed upon exposure of the insecticides to light.

In contrast to solution photolysis of parathion, exposure of the organophosphorus insecticides as a thin film to either sunlight or ultraviolet light resulted in only relatively small amounts of the delayed toxic compounds. Of the six dimethyl phosphorothioate or phosphorodithioate insecticides,

**Table XI. Photoalteration of Malathion Irradiated with Sunlight and Ultraviolet Light: Product Analysis**

irrad time, h	amount of product, nmol						
	1	2	3	5	12	13	14
Sunlight							
0.00	ND	ND	ND	ND	(18.0 ± 0.5) × 10 <sup>4</sup>	ND	ND
2.00	4.70 ± 0.0003	tr	0.62 ± 0.002	tr	(17.0 ± 1.0) × 10 <sup>4</sup>	tr	tr
4.00	3.20 ± 0.0010	tr	5.60 ± 0.0006	tr	(17.0 ± 0.7) × 10 <sup>4</sup>	tr	tr
6.00	8.20 ± 0.001	tr	5.00 ± 0.006	tr	(17.0 ± 0.4) × 10 <sup>4</sup>	tr	tr
8.00	4.40 ± 0.0010	tr	13.60 ± 0.003	tr	(17.0 ± 0.6) × 10 <sup>4</sup>	tr	tr
16.50	9.70 ± 0.0010	tr	19.30 ± 0.004	tr	(17.0 ± 0.3) × 10 <sup>4</sup>	tr	tr
25.00	14.40 ± 0.010	tr	19.00 ± 0.0006	tr	(19.0 ± 0.6) × 10 <sup>4</sup>	tr	tr
Ultraviolet Light							
0.00	ND	ND	ND	ND	(19.0 ± 0.6) × 10 <sup>4</sup>	ND	ND
5.00	ND	tr	3.60 ± 0.0004	0.50 ± 0.0004	(18.0 ± 0.5) × 10 <sup>4</sup>	tr	tr
16.00	tr	tr	1.60 ± 0.0020	1.10 ± 0.0001	(17.0 ± 0.9) × 10 <sup>4</sup>	tr	tr
22.00	16.20 ± 0.008	tr	1.40 ± 0.0020	3.60 ± 0.0010	(19.0 ± 0.9) × 10 <sup>4</sup>	tr	tr
28.00	9.40 ± 0.010	tr	1.60 ± 0.0020	2.00 ± 0.0009	(18.0 ± 0.2) × 10 <sup>4</sup>	tr	tr
41.00	tr	tr	0.10 ± 0.0020	0.9 ± 0.0009	(19.0 ± 0.1) × 10 <sup>4</sup>	tr	tr
46.00	7.70 ± 0.006	tr	3.4 ± 0.0001	2.30 ± 0.0008	(22.0 ± 0.9) × 10 <sup>4</sup>	tr	tr
48.00	2.50 ± 0.002	tr	tr	3.90 ± 0.0020	(20.0 ± 0.6) × 10 <sup>4</sup>	tr	tr
72.00	7.20 ± 0.0001	tr	tr	7.10 ± 0.0004	(16.0 ± 0.2) × 10 <sup>4</sup>	tr	tr

ticides examined, methyl parathion gave the largest amount of 1, followed by fenthion, methidathion, azinphos-methyl, malathion, and acephate. The light absorption maxima for these compounds are as follows (nm): methyl parathion, 273; fenthion, 253; methidathion, 252; azinphos-methyl, 220, 284; malathion, 253; acephate, 252.

This suggests that a primary factor determining photoalteration to 1 involves the ability of the compound to absorb ultraviolet radiation. Therefore, the low levels of the delayed toxic organophosphorus ester, 1, formed may be attributed to the wavelength mismatches between the spectral emissivity of our light sources and the  $\lambda_{\max}$  of the experimental phosphorothioate insecticides. This sets these organophosphorus insecticides apart from the pyrethroids whose various chromophoric groups result in an appreciable absorption at wavelengths in the visible region of the electromagnetic spectrum (Chen and Casida, 1969). Therefore, photoalterations are not expected to play as important a role in the environmental fate of these phosphorothioate insecticides as for most pyrethroids.

The molar extinction coefficients for the test insecticides were as follows ( $\text{mol}^{-1} \text{cm}^{-1}$ ;  $\lambda$ ) for methyl parathion, fenthion, methidathion, azinphos-methyl, malathion, and acephate, respectively:  $2.5 \times 10^6$ , 273 nm;  $0.3 \times 10^6$ , 253 nm;  $0.4 \times 10^6$ , 252 nm;  $0.4 \times 10^5$ , 220 nm;  $0.5 \times 10^5$ , 253 nm; and  $0.2 \times 10^4$ , 252 nm. In the same vein, the extent of formation of the delayed toxic organophosphorus esters generally followed the same trend.

One major experimental condition that sets this study apart from most pesticide photodecomposition studies is the complete absence of solvent mediation. This is because one of our prime considerations was to relate our findings with a situation on hydrophobic plant surfaces, such as leaves, in the field. Our data indicate that, in such an environment, photolytic formation of the delayed toxic organophosphorus esters will not feature prominently in the photodegradative fate of these phosphorothioate insecticides nor will it pose a serious threat of acute toxic hazards to farm workers. However, since a nonobservable effect level (NOEL) for these delayed toxic compounds has yet to be established, the possibilities for chronic hazards to farm workers remain an open question.

This study was carried out with purified compounds and, as such, the effects of photosensitizers present in formulations was not examined. Furthermore, the effects of photosensitizers present in leaves and other environmental matrices were also not studied. Investigations are currently going on in this area.

**Registry No.** 1, 152-20-5; 2, 22608-53-3; 3, 512-56-1; 4, 152-18-1; 5, 2953-29-9; 6, 298-00-0; 7, 950-35-6; 8, 597-89-7; 9, 55-38-9; 10, 950-37-8; 11, 86-50-0; 12, 121-75-5; 13, 1634-78-2; 14, 3344-12-5; 15, 30560-19-1; 16, 10265-92-6.

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