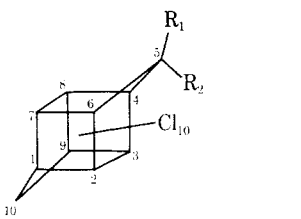
Identification of the Photoproducts of the Insecticides Mirex and Kepone

Earl G. Alley,* Bobby R. Layton, and James P. Minyard, Jr.

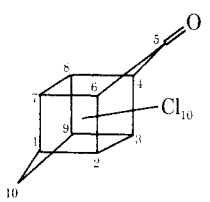
The photolysis of Kepone hydrate and the dimethyl ketal of Kepone in cyclohexane has been studied. Mass spectral, infrared, and nmr data were used to establish that the monodechlorinated photoproducts are 1,2,3,4,6,7,9,10,10-nonachloro-5,5-dihydroxypentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane for the hydrate and 1,2,3,4,6,7,9,10,10-nonachloro-5,5-dimethoxypentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane for the ketal. The chemical conversion of these compounds to the corresponding Mirex derivative was used to establish the structure of a monohydro photoproduct of Mirex.

Both Mirex (1) (dodecachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane) and Kepone (4) (decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one) have been used as insecticides. The reactivity of the carbonyl group of Kepone has been demonstrated by Dilling *et al.* (1967), Griffin and Price (1964), and Gilbert *et al.* (1966). However, Mirex is inert to many common acids, bases, and oxidizing and reducing agents (McBee *et al.*, 1956). Eaton *et al.* (1960) found that both 1 and 4 are thermally stable. Furthermore, it has been suggested that the chlorocarbon Mirex presents a possible environmental problem (Lowe *et al.*, 1971; Ludke *et al.*, 1971; Van Valin *et al.*, 1968).

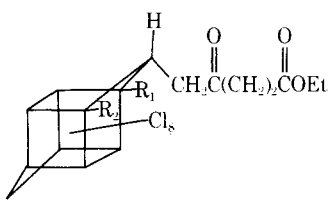
The photodecomposition of Mirex (1) (Alley *et al.*, 1973) and the related compound Kelevan (5) (Parlar *et al.*, 1972) has been reported. In both cases, chlorine atoms were replaced with hydrogen atoms. Explicit structure assignments were not made for the Mirex photoproducts. The assignment of structures **6a** and **6b** to the Kelevan photoproducts (Parlar *et al.*, 1972) by mass spectrometry was facilitated by the reduced symmetry created by the presence of the hydroxyl and levulinate groups in these compounds.



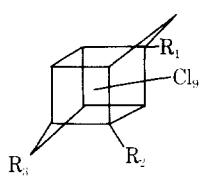
1, $R_1 = R_2 = Cl$
2, $R_1 = R_2 = OH$
3, $R_1 = R_2 = OCH_3$



4



5, $R_1 = R_2 = Cl$
6a, $R_1 = H$; $R_2 = Cl$
6b, $R_1 = R_2 = H$



7, $R_1 = R_2 = Cl$; $R_3 = H$
8, $R_1 = R_3 = Cl$; $R_2 = H$
9, $R_1 = H$; $R_2 = R_3 = Cl$

Of the three possible monohydro isomers of Mirex (7, 8, and 9), Dilling *et al.* (1967) unambiguously synthesized compound 7 from Kepone. This isomer was proved to be absent when Mirex was irradiated in hydrocarbon solvents. Dilling *et al.* (1967) also prepared another monohydro isomer, and comparison of the spectra and chromatograms of this compound with the monohydro photoproduct of Mirex revealed their identity. The discrepancies in the reported infrared spectra (Alley *et al.*, 1973) can be explained by impurities present in Dillings's sample.

Mississippi State Chemical Laboratory, Mississippi State, Mississippi 39762.

Direct synthesis of specific Mirex derivatives, other than 7, was not possible because nothing was known about the chemical reactivity of the different chlorine atoms in Mirex or Kepone. Furthermore, neither infrared, mass spectral, nor nmr data from the photoproduct of Mirex provided sufficient information to distinguish between the remaining possibilities (8 and 9).

The symmetry properties of Kepone and its derivatives are different from those of Mirex, and so the mass spectra of some of their photodechlorination products are unique (Table I). From these data and the nmr spectra of these compounds one should be able to differentiate among the four possible monohydro derivatives of Kepone. Additionally, direct routes for chemical conversion of Kepone and some of its derivatives to Mirex have been reported (Griffin and Price, 1964; Dilling *et al.*, 1967); therefore, specific monohydro derivatives can be obtained from the corresponding Kepone derivatives.

In this investigation some of the photochemistry of Kepone hydrate (2) and of the dimethyl ketal of Kepone, 3, was studied. The assignments of the structures of the photoproducts of 2 and 3 have been made from their mass spectra. Chemical conversion of the primary photoproducts of these Kepone derivatives to their corresponding Mirex analogs produces compounds identical with the Mirex photoproducts, and so the geometry of the monohydro photoproduct of Mirex can be assigned.

RESULTS AND DISCUSSION

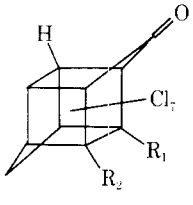
Ultraviolet irradiation of Kepone hydrate (2) in cyclohexane gave two major products. Attempts to isolate these photoproducts by preparative gas chromatography or liquid–solid adsorption chromatography failed. The mass spectra obtained with a gas chromatograph interfaced to a mass spectrometer were for the ketones rather than the *gem*-diols because dehydration occurred during the gas chromatographic separation of 2 and its photoproducts. The mass spectral analysis of these ketones indicated that the two photoproducts of Kepone hydrate (2) have the molecular formulas $C_{10}Cl_9H_3O_2$ and $C_{10}Cl_8H_4O_2$.

The mass spectral fragmentation modes of Kepone are analogous to those for Mirex (Dilling and Dilling, 1967). When the pentacyclic skeleton of Kepone is cleaved, $C_5Cl_6^+$ and $C_5Cl_4O^+$ fragments result. Within an isotopic cluster, the number of mass peaks and their intensities are determined by the number of chlorine atoms present and the natural abundance of the chlorine isotopes; therefore, the assignment of the number of chlorines contributing to an ion cluster is unambiguous. The monohydro derivative of Kepone had major peaks for $C_5Cl_5H^+$, $C_5Cl_6^+$, $C_5Cl_4O^+$, and $C_5Cl_3HO^+$ ions (fragments from the cleavage of the pentacyclic carbon skeleton) and $C_5Cl_5^+$ ions (dechlorination of the $C_5Cl_6^+$ fragments). Of the possible monohydro isomers, only structure 10 (1,2,3,4,6,7,9,10,10-nonachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one could give these ions upon fragmentation (Table I).

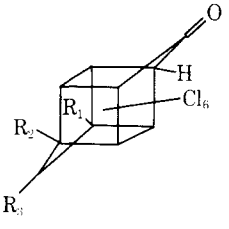
Table I. C_5 Cleavage Fragments of the Kepone Compounds

Compound	Positions of the hydrogens (see structure 4)	Predicted cyclopentadiene and cyclopentadienone fragments					
		$C_5Cl_6^+$	$C_5Cl_5H^+$	$C_5Cl_4H_2^+$	$C_5Cl_4O^+$	$C_5Cl_3HO^+$	$C_5Cl_2H_2O^+$
	10	–[a]	+	–	+	–	–
	9	–	+	–	+	–	–
$C_{10}Cl_9HO$	8	+	+	–	+	+	–
	6	+	–	–	–	+	–
	Obsd for dehydrated photoproduct	+	+	–	+	+	–
	(6,4)	+	–	–	–	–	+
	(10,6), (9,6), (9,4), (8,2), (8,3)	–	+	–	–	+	–
$C_{10}Cl_8H_2O$	(10,10), (10,9), (9,1)	–	–	+	+	–	–
	(8,6), (8,4)	+	+	–	–	+	+
	(8,7)	+	–	+	+	–	+
	(10,8), (9,8), (9,7)	–	+	+	+	+	–
	Obsd for dehydrated photoproduct	–	+	–	–	+	–

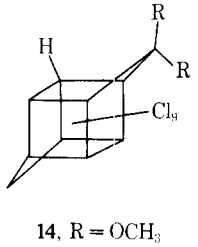
[a] +, present; –, not present.



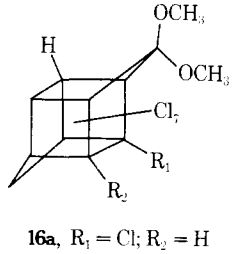
10, $R_1 = R_2 = Cl$
11a, $R_1 = Cl$; $R_2 = H$
11b, $R_1 = H$; $R_2 = Cl$



12a, $R_1 = R_3 = Cl$; $R_2 = H$
12b, $R_1 = H$; $R_2 = R_3 = Cl$
13, $R_1 = R_2 = Cl$; $R_3 = H$



14, $R = OCH_3$
15, $R = OH$



16a, $R_1 = Cl$; $R_2 = H$
16b, $R_1 = H$; $R_2 = Cl$

The mass spectrum of the dihydro derivative of Kepone had major peaks for $C_5Cl_5H^+$ ions, but none for $C_5Cl_6^+$, $C_5Cl_4H_2^+$, $C_5Cl_5^-$, or $C_5Cl_3H_2^+$ ions. This fragmentation pattern could be obtained only from **11a, 11b, 12a, 12b,** or **13** (Table I).

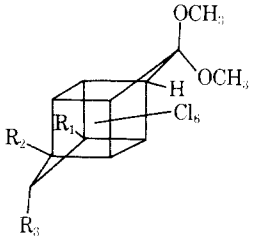
Since the photoproducts of Kepone hydrate could not be isolated, the photochemistry of another derivative of Kepone (the dimethyl ketal) was investigated. Two photoproducts were formed, a monohydro and a dihydro derivative. The mass spectrum of the monohydro derivative of the ketal contained both $C_5Cl_6^+$ and $C_5Cl_5H^+$ ions. In addition, ions attributable to the oxygen-containing fragments were present but their analysis was complicated by further fragmentation and overlap of the resultant ions. Arguments similar to those for **10** require that this compound be assigned structure **14** (1,2,3,4,6,7,9,10,10-nonachloro-5,5-dimethoxypentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane). The infrared spectrum of compound **14** did not have a band at 1600 cm^{-1} (C=C) which excludes the possibility that ring opening had occurred. This assignment is further supported by the nmr spectrum of this compound which had three sharp singlets: δ 3.56 (1), 3.54 (3), and 3.51 (3). Of the possible isomers, only **14** is consistent with these nmr data. The other isomers are expected to have a single methyl resonance or a resonance at about δ 4.3 (Dilling *et al.*, 1967) for a hydrogen α to a chlorine.

The mass spectrum of the dihydro photoproduct of the dimethyl ketal had peaks for $C_5Cl_5H^+$ ions but none for $C_5Cl_4H_2^+$ ions. Ketals with structures **16a, 16b, 17a, 17b,** and **18** are the only possibilities consistent with these data (Table I). The nmr spectrum of this photoproduct had only a slightly broadened peak at δ 3.56. Structure **18** has a hydrogen and chlorine attached to the same carbon atom and the chemical shift of this hydrogen should be about δ 4.3 (Dilling *et al.*, 1967); therefore it may be eliminated from consideration.

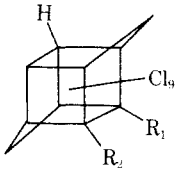
Hydrolysis of the monohydro photoproduct of the ketal gave a compound whose mass spectrum and gas chromatographic retention time were identical with those for the monohydro photoproduct of Kepone hydrate (**15**). Treatment of **15** with phosphorus pentachloride gave a substance whose infrared spectrum was identical with that of the Mirex photoproduct. The infrared spectra of the dihydro photoproduct of Mirex (**19a** or **19b**) and of the Mirex derivative synthesized from the ketal dihydro photoproduct were also identical. Additionally, a mixture of the two photoproducts of Kepone hydrate (**2**) was converted to the corresponding mono- and dihydro derivatives of Mirex by treatment with phosphorus pentachloride. The resulting derivatives were isolated by liquid-solid adsorption chromatography. The nmr and infrared spectra of these compounds were identical with those for the corresponding Mirex photoproducts. These photoproducts were reported earlier (Alley *et al.*, 1973) and characterized by their spectra and elemental analyses.

The unambiguous assignment of structures to the photoproducts of the Kepone derivatives coupled with their chemical conversion to the corresponding Mirex derivatives unequivocally establish that **8** is the structure of the monohydro photoproduct of Mirex. Since compound **8** was shown to be a precursor of the dihydro photoproduct of Mirex (Alley *et al.*, 1973), it also follows that the possible structures for the dihydro photoproducts of Kepone hydrate are **20a** or **20b** and for the ketal **16a** or **16b.**

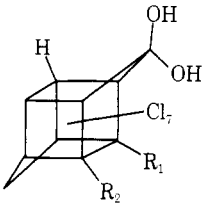
The photoreduction of Kelevan (**5**) (Parlar *et al.*, 1972) occurred at a different position than that observed for Mirex, Kepone hydrate, or the dimethyl ketal of Kepone.



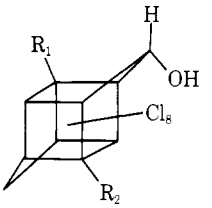
17a, $R_1 = R_3 = Cl$; $R_2 = H$
17b, $R_1 = H$; $R_2 = R_3 = Cl$
18, $R_1 = R_2 = Cl$; $R_3 = H$



19a, $R_1 = Cl$; $R_2 = H$
19b, $R_1 = H$; $R_2 = Cl$



20a, $R_1 = Cl; R_2 = H$
20b, $R_1 = H; R_2 = Cl$



21, $R_1 = R_2 = Cl$
22a, $R_1 = H; R_2 = Cl$
22b, $R_1 = Cl; R_2 = H$

Kelevan differs from Mirex and the hydrate and ketal of Kepone by virtue of the presence of one *vs.* two electronegative atoms attached to one of the methylene bridges and the attachment of the levulinate group to one of the methylene bridges of Kelevan. Additionally, the solvent for the Kelevan photolysis was acetone, whereas hydrocarbon solvents were employed in the photolysis of Mirex and the other Kepone derivatives. Neither the solvent system nor the differences caused by the presence of one *vs.* two electronegative groups proved to be the controlling factor in the stereochemistry of these reactions. Mass spectral evidence showed that irradiation of **21** in acetone produced either compound **22a** or **22b** or a mixture of these compounds. Since the stereochemistry of this reaction is like that of Mirex and Kepone rather than Kelevan, the properties of the levulinate group must control the route of the reaction in the photoreduction of Kelevan.

EXPERIMENTAL SECTION

Technical Kepone donated by Allied Chemical Corp. was recrystallized twice from benzene. Reagent grade cyclohexane was further purified by fractional distillation.

The reactions were monitored with a Varian Aerograph Model 1400 gas chromatograph equipped with a flame ionization detector and the following columns: 5% SE-30 on ABS 80–90 and 0.35% diethylene glycol succinate (DEGS) on 100–120 mesh textured glass beads.

The spectra were measured with a Perkin-Elmer Model 457 infrared spectrophotometer, a JEOL Model MH-60II nuclear magnetic resonance spectrometer, and a Perkin-Elmer Model 270 mass spectrometer interfaced to a gas chromatograph with a 50-ft OV-1 support coated, open tubular (SCOT) column.

The compounds were placed in an Ace photochemical reactor and irradiated with a Hanovia 450-W, high-pressure mercury lamp. The photochemical reactor and quartz immersion well were water cooled. The solutions were stirred magnetically and continuously flushed with nitrogen.

Photolysis of Decachloro-5,5-dimethoxypentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (3). The ketal **3** was prepared from compound **4** by the method of Griffin and Price (1964). A solution of **3** (0.7 g) in 300 ml of cyclohexane was irradiated until approximately 80% of the ketal had disappeared (6 hr). It was concentrated to 50 ml and chromatographed on alumina. Elution with cyclohexane produced 0.12 g (17% yield) of compound **14** (a colorless glass). Due to the physical state of this material, the solvent could not be removed completely enough to obtain satisfactory elemental analysis. The purified product had the following spectra: ir (CS_2, cm^{-1}) 3020 (w), 2980 (w), 2940 (m), 2830 (w), 1250 (s), 1225 (sh), 1220 (s), 1192 (s), 1185 (m), 1160 (m), 1150 (m), 1140 (m), 1117 (s), 1108 (s), 1100 (sh), 1080 (w), 1057 (w), 1049 (m), 1045 (sh), 1038 (m), 1022 (m), 1005 (sh), 995 (m), 975 (w), 955 (w), 925 (w), 920 (sh), 890 (w), 850 (m), 845 (sh), 830 (m), 785 (w), 770 (w), 750 (w), 730 (w), 670 (w), 655 (m), 645 (m), 605 (m), 583 (m), 575 (w), 560 (m), 555 (sh), 540 (w), 500 (m); nmr ($CDCl_3$, TMS) δ 3.56 (1), 3.53 (3), 3.51 (3). The mass spectrum had ion clusters for $C_{12}Cl_9H_7O_2^+$ ions (parent), $C_{12}Cl_8H_7O_2^+$ ions (dechlorination of the parent), $C_5Cl_6^+$ and $C_5Cl_5H^+$ ions (fragments from the cleavage of the pentacyclic carbon skeleton), $C_5Cl_5^+$ ions (dechlorination of the $C_5Cl_6^-$ ions), and a number of less informative ions.

Further elution of the alumina column with cyclohexane produced an additional 60 mg (7.5% yield) of material. Glpc analysis indicated that it was a 1:6 mixture of compound **14** and another photoproduct whose retention time relative to **6** was 0.49 on SE-30 (240°). The nmr spectrum of this material had a sharp singlet (2 Hz at half-height, δ 3.56 (TMS, $CDCl_3$)). The mass spectrum of **16** (**a** or **b**) had ion clusters for $C_{12}Cl_8H_8O_2^+$ ions (parent), $C_{12}Cl_7H_8O_2^+$ ions (dechlorination of the parent), and $C_5Cl_5H^+$ ions (fragments from the cleavage of the pentacyclic carbon skeleton). No ions were observed for $C_5Cl_6^+$ or $C_5Cl_4H_2^+$ fragments.

Preparation of 1,2,3,4,6,7,9,10,10-Nonachloro-5,5-dihydroxypentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (15). Hydriodic acid (10 ml of a 47% solution) was added slowly to a solution of compound **14** in 25 ml of acetic anhydride and then heated at reflux for 36 hr. The reaction mixture was cooled, water was added, and the resulting mixture extracted with methylene chloride. The organic phase was washed with a saturated solution of sodium bicarbonate and then with saturated aqueous sodium thiosulfate. After drying over anhydrous sodium sulfate, the solvent was removed by evaporation. This material (0.112 g, 99% yield) had the following spectra: ir (CS_2, cm^{-1}) 3530 (s), 3020 (w), 2970 (w), 2920 (m), 2840 (w), 1335 (w), 1245 (m), 1222 (s), 1220 (sh), 1210 (w), 1180 (sh), 1175 (s), 1165 (s), 1140 (s), 1105 (s), 1085 (m), 1070 (sh), 1060 (w), 1040 (w), 1025 (w), 1010 (m), 975 (w), 935 (w), 890 (w), 845 (m), 820 (w), 810 (w), 782 (w), 775 (w), 765 (w), 755 (s), 730 (w), 660 (m), 650 (m), 620 (m), 580 (m), 555 (m), 540 (w), 490 (m); nmr (TMS, $CDCl_3$) δ 3.34 (2) (4 Hz at half-height), 3.63 (1) (1.5 Hz at half-height). The mass spectrum included ion clusters for $C_{10}Cl_9HO^+$ ions (dehydrated parent), for $C_5Cl_6^+$, $C_5Cl_5H^+$, $C_5Cl_4O^+$, and $C_5Cl_3HO^+$ ions (fragments from the cleavage of the pentacyclic carbon skeleton), and for $C_5Cl_5^+$ ions (dechlorination of the $C_5Cl_6^+$ fragments).

Photolysis of Decachloro-5,5-dihydroxypentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (2). A solution of **2** (1.0 g) in 300 ml of cyclohexane was irradiated for 6 hr. Repeated attempts to separate the products by preparative gas chromatography and column chromatography failed. However, the glpc retention time (0.75 relative to **2**) of one of the products was identical with that of compound **15** prepared by the above method. The mass spectrum of this compound was obtained from a mass spectrometer interfaced with a gas chromatograph (50-ft SCOT column, 190°). The mass spectrum was identical with that of **15** prepared by hydrolysis of the corresponding ketal.

The photolysis of **2** produced a second compound which had a retention time relative to **4** of 0.56 (SE-30 at 220°). Attempts to isolate this compound by chromatography failed; therefore, it was characterized by mass spectrometry. The mass spectrum included ion clusters for $C_{10}Cl_8H_2O^+$ (dehydrated parent) and for $C_5Cl_5H^+$ and $C_5Cl_3HO^+$ (fragments from the cleavage of the pentacyclic skeleton). No ions were observed for $C_5Cl_6^+$ or $C_5Cl_4H_2^+$.

Preparation of 1,2,3,4,5,5,6,7,9,10,10-Undecachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decane (8). Phosphorus pentachloride (1.0 g) and 0.112 g of compound **15** in 50 ml of tetrachloroethylene were heated at reflux temperature for 36 hr. Preliminary purification was accomplished by passing the solution through a 4-in. layer of Florisil. After the solvent had been removed with a rotary evaporator, 0.121 g (94% yield) of **8** was obtained. Its infrared spectrum was identical with the monohydro photoproduct of **1**.

Furthermore, the photolysis products of **2**, a mixture of

compounds 15 and 20 (a or b), were converted to the corresponding chlorides with phosphorus pentachloride. The components of the resulting mixture were separated by column chromatography (alumina eluted with cyclohexane). These compounds had ir spectra identical with the photoproducts of 1.

Photolysis of 1,2,3,4,6,7,8,9,10,10-Decachloropentacyclo[5.3.0.$0^{2,6}$.$0^{3,9}$.$0^{4,8}$]decan-5-ol (21). Compound 21 was prepared from Kepone by reduction with lithium aluminum hydride (Allied Chemical Corp., 1964). A solution of 21 (0.1 g) in 20 ml of acetone was irradiated for 4 hr. The glpc analysis indicated that one product was formed with retention time 0.75 relative to 21 (SE-30, 240°). The mass spectrum of this compound was obtained from a mass spectrometer interfaced with a gas chromatograph (8-ft SE-30, 240°). The mass spectrum included ion clusters for $C_{10}Cl_9H_3O^+$ (parent), for $C_5Cl_6^+$ and $C_5Cl_5H^+$ (from cleavage of the pentacyclic carbon skeleton), and for $C_5Cl_5^+$ ions (dechlorination of the $C_5Cl_6^+$ fragments).

ACKNOWLEDGMENT

The authors wish to express their gratitude to Dr. W. L. Dilling for the gift of a sample of the Mirex derivative.

LITERATURE CITED

Alley, E. G., Dollar, D. A., Layton, B. R., Minyard, J. P., Jr., *J. Agr. Food Chem.* **21**, 138 (1973).
Allied Chemical Corp., Netherland Appl. 6,400,728 (1964); *Chem. Abstr.* **64**, 11705e (1965).
Dilling, W. L., Braendlin, H. P., McBee, E. T., *Tetrahedron* **23**, 1211 (1967).
Dilling, W. L., Dilling, M. L., *Tetrahedron* **23**, 1225 (1967).
Eaton, P., Carlson, E., Lombardo, P., Yates, P., *J. Org. Chem.* **25**, 1225 (1960).
Gilbert, E. E., Lombardo, P., Rumanowski, E. J., Walker, G. L., *J. Agr. Food Chem.* **14**, 111 (1966).
Griffin, G. W., Price, A. K., *J. Org. Chem.* **29**, 3192 (1964).
Lowe, J. I., Parish, P. R., Wilson, A. J., Jr., Wilson, P. D., Duke, T. A., presented in part at the 36th North American Wildlife and Natural Resource Conference, Portland, Ore., March, 1971.
Ludke, G. L., Finley, M. T., Lusk, C., *Bull. Environ. Contam. Toxicol.* **6**, 89 (1971).
McBee, E. T., Roberts, C. W., Idol, J. D., Jr., Earle, R. H., Jr., *J. Amer. Chem. Soc.* **78**, 1511 (1956).
Parlar, H., Klein, W., Korte, F., *Chemosphere* **1**, 129 (1972).
Van Valin, C. C., Andrews, A. K., Eller, L. L., *Trans. Amer. Fish Soc.* **97**, 185 (1968).

Received for review October 18, 1973. Accepted January 7, 1974. The authors are indebted to the Entomology Research Division of the U. S. Department of Agriculture for financial support for this research.

Analysis of Dimethoate-Treated Grapes for the *N*-Hydroxymethyl and De-*N*-methyl Metabolites and for Their Sugar Adducts

William A. Steller* and William W. Brand

Gas-liquid chromatographic (glc) methods are presented for the determination of de-*N*-methyl dimethoate, *N*-hydroxymethyl dimethoate, de-*N*-methyl dimethoxon, *N*-hydroxymethyl dimethoxon, and the *O*-glucoside of *N*-hydroxymethyl dimethoate in grapes at levels down to 0.05 ppm for each compound. Recovery values for all these compounds are presented. Analyses of field-treated grape samples harvested 28 days after the last application of dimethoate showed no residues of any of these compounds at or above the validated sensitivity limit (0.05 ppm) of the method, indicating that they do not constitute a significant part of the dimethoate-related residues in grapes. Synthesis and isolation procedures used to obtain *N*-hydroxymethyl dimethoate, *N*-hydroxymethyl dimethoxon, de-*N*-methyl dimethoxon, and *N*-hydroxymethyl dimethoate *O*-glucoside are also described.

Dimethoate (I) [*O,O*-dimethyl *S*-(methylcarbamoyl)-methyl phosphorodithioate], the active ingredient in Cygon systemic 25 insecticide (trademark of American Cyanamid Co.), is an organophosphate insecticide effective for the control of a wide variety of pests on crops, including control of Pacific spider mite and grape leafhopper on grapes as well as for house fly control when applied as a residual spray to various surfaces. Previously reported work on the metabolism of dimethoate in plants had shown oxidation to dimethoxon (II) as the only mechanism yielding toxic residues. The main degradative pathways elucidated in this early work were to the nontoxic de-*O*-methyl dimethoate, dimethoate carboxylic acid, and oxy-carboxy dimethoate, as well as to the hydrolysis products resulting from cleavage of the P–S and S–C bonds of the molecule. The metabolism of dimethoate in plants has been reviewed by Lucier and Menzer (1968). Because of this metabolic pattern, the recommended methods of analysis for total toxic residues in crops treated with dimethoate measure only dimethoate and dimethoxon as described by Steller and Pasarela (1972).

Agricultural Division, American Cyanamid Company, Princeton, New Jersey 08540.

Recently, however, Lucier and Menzer (1970) reported finding trace quantities (0.08 ppm maximum) of de-*N*-methyl dimethoate (III), de-*N*-methyl dimethoxon (V), *N*-hydroxymethyl dimethoate (IV), and *N*-hydroxymethyl dimethoxon (VI) in bean plants treated by foliar application with 15 ppm of dimethoate-*carbonyl*-^{14}C. Six days after treatment 77% of the recoverable radioactivity was present as water-soluble compounds. Acidic and enzymatic hydrolyses of this water-soluble fraction demonstrated the absence of any *N*-hydroxymethyl dimethoate or *N*-hydroxymethyl dimethoxon conjugates in the bean plants as reported by Lucier by private communication (1971). Even though no conjugates were found in bean plants, the possible presence of even small quantities of de-*N*-methyl dimethoate, de-*N*-methyl dimethoxon, *N*-hydroxymethyl dimethoate, and *N*-hydroxymethyl dimethoxon in the bean plants was considered sufficient reason to suggest the possibility of a potential pool of *N*-hydroxymethyl dimethoate sugar adducts in grapes. Giang and Beckman (1968) reported that sugar adducts of two insecticides, Bidrin and Azodrin (with structures similar to dimethoate), were found when these compounds were applied to plants, but Elgar and MacDonald (1966) reported that sugar adducts were found to be absent from fruits (apples and oranges) treated with Bidrin.