Figure 1. Degradation of RH-0994 in water in the dark. The RH-0994 sulfone and phenol sulfone analogues either were not formed under the conditions of study or were generated in amounts too low for detection.

stable under moderately acidic aqueous conditions but is rapidly degraded at alkaline pH, where hydrolysis of the phosphorus–O–phenyl ester linkage is the major initial degradation step (Table II). Many organic phosphate insecticides are known to be readily susceptible to base- but not acid-catalyzed ester hydrolysis (O'Brien, 1967); thus our data on the pH-dependent degradation of RH-0994 are not at all surprising.

The finding that RH-0994 and its phenolic hydrolysis product readily oxidized to sulfoxide analogues during our sample preparation and analysis procedures suggests that caution may be required in the development and utilization

of analytical methods for this compound and its derivatives. Alternatively, because sulfides, sulfoxides, and sulfones in a given series are usually considered to be toxicologically equivalent from a regulatory standpoint (Ivie and Bandal, 1981), the sulfur oxidation artifacts observed in the current study may be of little or no significance regarding the development of analytical methods for quantitation of RH-0994 residues. At any rate, we in our studies fortuitously minimized such problems by the addition of unlabeled RH-0994 and its analogues prior to extraction and analysis. With these additions, oxidation of RH-0994 during sample workup appeared to be minimal, on the basis of 0-day data (Table II). However, it is possible that oxidation of phenol to phenol sulfoxide may have occurred during sample workup; thus caution in accepting these data as absolute values is warranted.

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Metabolism of *N*-(2,3-Dichlorophenyl)-3,4,5,6-tetrachlorophthalamic Acid (Techlofthalam) in Paddy Soil and Rice

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The metabolism of the bactericide *N*-(2,3-dichlorophenyl)-3,4,5,6-tetrachlorophthalamic acid, techlofthalam, has been studied, under controlled conditions, in paddy soil and after application to rice plants by using the ¹⁴C-labeled compound. Reductive dechlorination of the tetrachlorophthalamic acid moiety was shown to be the major degradative pathway in paddy soil stored in laboratory flasks. Monodechlorinated products were detected after 2 weeks of incubation, and after 32 weeks more than 90% of the extractable radioactivity, equivalent to about 30% of the applied radioactivity, was associated with two or possibly more monodechlorinated products. Nine percent of the applied radioactivity was converted to ¹⁴CO₂ during 32 weeks. The imide of techlofthalam was a minor metabolite in paddy soil but was the major transformation product detected in rice leaves treated with [¹⁴C]techlofthalam.

The compound *N*-(2,3-dichlorophenyl)-3,4,5,6-tetrachlorophthalamic acid, techlofthalam, is a new systemic

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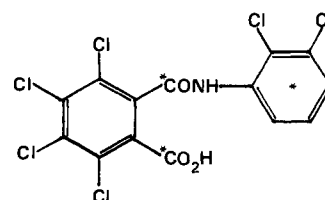
bactericide for the control of bacterial leaf blight (*Xanthomonas oryzae*) in rice (Nakagami et al., 1980). Techlofthalam possesses low acute mammalian toxicity with

oral LD_{50} values of about 2000 mg/kg in rats and mice (Ishida, 1975). The synthesis of [^{14}C]techlofthalam and its metabolism in the rat have been described (Kirkpatrick et al., 1981). This paper describes studies on the metabolism of [^{14}C]techlofthalam in paddy soil and in rice plants, both under controlled conditions, in a plant growth room. These studies were designed to obtain information on the fate of techlofthalam and the nature of the residues which would be likely to occur after normal field use of the pesticide. To allow for possible metabolic cleavage of the molecule, the studies were conducted using techlofthalam labeled in both the tetrachlorophthalamic acid and the dichloroaniline groups.

EQUIPMENT AND METHODS

The methods used for liquid scintillation counting (LSC), combustion analysis (CA), thin-layer chromatography (TLC), and the location and quantitation of radioactive components on TLC plates were as described previously (Kirkpatrick et al., 1981). TLC solvent systems used in this study for separation of radioactive components in soil and plant extracts were (a) chloroform-methanol-98% formic acid (80:20:1 v/v) and (b) ethyl acetate-2-propanol-35% ammonia (9:7:4 v/v).

Mass spectra were recorded on a VG Micromass 16F mass spectrometer (VG Analytical Ltd., U.K.). Electron impact spectra were recorded at an ion source temperature of 200–220 °C, an electron beam energy of 70 eV, and a trap current of 100 μA. Samples were introduced either on the direct insertion probe, which was heated gradually from 30 to 250 °C, or via a Pye 104 gas chromatograph interfaced to the mass spectrometer through a single-stage jet separator. Gas chromatographic separations were accomplished on a 200 × 0.4 cm i.d. glass column packed with 3% OV 17 on Chromosorb W (HP, 80–100 mesh). The carrier gas was helium at a flow rate of 20 mL/min, and the column temperature was 280 °C. The integrated ion current profile in the mass range m/e 300–500 was monitored.

EXPERIMENTAL SECTION

Synthesis of [^{14}C]Techlofthalam. [*carbonyl*-^{14}C]-Techlofthalam, specific activity 15 mCi/mmol, and [*2,3-dichlorophenyl*-U-^{14}C]techlofthalam, specific activity 20 mCi/mmol, were prepared as previously described (Kirkpatrick et al., 1981).

Nonradioactive techlofthalam imide was supplied by the
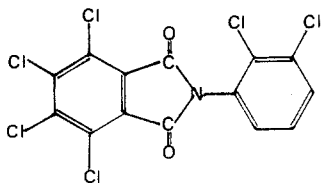
Sankyo Co. Ltd., Japan. The preparation of the imide from techlofthalam has been described (Kirkpatrick et al., 1981).

Studies with Soil. A silty loam textured paddy soil was obtained from Japan. Soil texture, organic matter content (3.6%), and pH (6.5) were determined by the Soil Science Department, Ministry of Agriculture, Fisheries and Food, Cambridge, U.K. The soil was not allowed to dry out during transport and storage, and its water content was determined by drying small samples. Conditions of soil storage during the experiment were designed to simulate a paddy field environment. The soil was dispensed into individual glass 250-mL conical flasks so as to give 50 g of soil on a dry weight basis in each flask. Distilled water

was added to bring the water content of each flask up to 150% of the soil dry weight. This was sufficient to completely flood the soil to a depth of 1–2 cm. This water content was maintained throughout the study by the addition of further distilled water at intervals. Plugs of cotton wool were inserted into the necks of the flasks which were then acclimated for 1 month before use. The flasks were stored under controlled conditions with a 16-h light period, 8 klx intensity, and day–night temperatures of 23 and 19 °C, respectively.

A solution of [^{14}C]techlofthalam in methanol was prepared containing equal quantities, in terms of radioactivity, of the two radiolabeled forms. This solution was added to the water above the soil in the flasks at a rate of 50 μL/flask. The flasks were then shaken vigorously. The application rate was 1 μg of techlofthalam/g of soil (dry weight). Duplicate flasks were removed for analysis at 1, 2, 4, 8, 16, and 32 weeks after application. For the purpose of obtaining larger amounts of metabolites for possible identification, some additional soil flasks were treated at a rate of 10 μg of techlofthalam/g of soil. These flasks were analysed at 2, 4, and 48 weeks after application.

Analysis of Soil Samples. Supernatant water was separated by centrifugation. Soil samples were then extracted sequentially with acetone, methanol, and water in an ultrasonic bath (15 min; 25 °C) and additionally with methanol in a Soxhlet apparatus (4 h). It was shown that the Soxhlet treatment did not affect radioactive metabolites in soil extracts. Radioactivity was measured in all liquid samples by LSC and in the solid residue remaining after extraction by CA, followed by LSC.

The supernatant water, acetone, and methanol extracts from duplicate samples were pooled separately and concentrated on a rotary film evaporator at 35 °C, and the concentrated extracts were analyzed by TLC in solvent systems a and b.

For the identification of radioactive metabolites in soil, methanol extracts of the higher application rate soil samples were subjected to preparative layer (2-mm thickness) chromatography in solvent system a. After autoradiography, the band of silica gel corresponding to the major zone of radioactivity was removed from the plate and extracted with methanol. This extract was subjected to preparative layer chromatography in solvent system b. Bands of silica corresponding to zones of radioactivity were removed separately and extracted with methanol. These methanol extracts were rechromatographed in solvent system a to obtain purer samples of metabolites which were then subjected to mass spectrometry.

Measurement of Volatile Radioactivity Produced in Soil. Duplicate soil samples, treated with [^{14}C]techlofthalam, were stored in closed flasks fitted with two stopcocks. At 32 weeks after application, the atmospheric contents of the flasks were drawn through a flow system consisting of one trap containing 2% aqueous sodium hydroxide to trap $^{14}CO_2$, followed by a catalytic tube (containing cupric oxide and manganese dioxide at 700 °C) to oxidize other volatile organic compounds to $^{14}CO_2$, followed by two further traps of 2% aqueous sodium hydroxide. Radioactivity was measured in the contents of all traps by LSC. The efficiency of the catalytic tube was checked by using [^{14}C]ethanol.

Studies with Rice. Rice plants (variety Kinmaze) were grown in pots of compost in a plant growth room. Light and temperature conditions were the same as those for the soil samples. Humidity was 70–90%. A suspension of [^{14}C]techlofthalam (1 mg/mL) in a 300-ppm solution of Tween 20 was prepared containing equal quantities of the

Table I. Radioactivity in Extracts and Residues of Soil Samples after Application of [^{14}C]Techlofthalam at a Rate of 1 μg/g of Soil[a]

time after applica-tion, weeks	super-natant water	extracts	residue	total
1	15.2	59.8	9.8	84.8
	18.3	56.0	7.6	81.9
2	15.8	68.5	13.6	97.9
	21.3	62.9	10.6	94.8
4	14.6	67.8	13.9	96.3
	15.2	53.4	22.9	91.5
8	16.4	49.5	23.3	89.2
	14.7	53.8	21.1	89.6
16	8.9	50.6	28.2	87.7
	2.8	27.4	58.2	88.4
32	4.6	27.0	28.9	60.5
	1.6	38.8	27.3	67.7

[a] Results are expressed as percent applied radioactivity and are given for duplicate samples at each time.

Table II. Proportions[a] of Radioactive Components in Soil Extracts

time after applica-tion, weeks	sam-ple[b]	radioactive component no. (approx. R_f)[c]				
		1 (0.64)	2 (0.71)	3[d] (0.78)	4 (0.86)	5 (0.95)
1	SW	ND[e]	1	15	0.3	ND
	OE	0.2	1	53	1	0.2
2	SW	ND	2	16	0.4	ND
	OE	ND	6	58	1	ND
4	SW	0.4	4	10	0.3	ND
	OE	0.4	11	44	1	0.2
8	SW	ND	5	10	ND	ND
	OE	0.7	12	37	0.4	0.4
16	SW	0.2	2	3	0.1	ND
	OE	ND	10	23	0.2	2
32	SW	0.7	2	ND	ND	ND
	OE	11	19	0.6	0.1	0.8

[a] Results are expressed as percent radioactivity applied to soil. [b] SW = supernatant water; OE = organic extracts. [c] Solvent system b. [d] Corresponds to techlofthalam. [e] ND = not detected.

two radiolabeled forms. Aliquots of this suspension were applied to selected leaves of individual plants by using a sable hair brush. Duplicate plants were analyzed at each of the following times after application: 1, 3, 7, 15, and 30 days.

Analysis of Rice Plants. Plants were analyzed individually and were separated into treated and untreated leaves. The leaves were placed in a stoppered measuring cylinder and shaken with acetone (50–200 mL) for 30 s (acetone wash). The leaves were then extracted twice by homogenization with acetone in a blender. Radioactivity was measured in washes and extracts by LSC and in the insoluble residue by CA, followed by LSC. Acetone extracts were evaporated to dryness, and the residual radioactivity was partitioned between water and chloroform. Radioactivity was measured in both phases. The chloroform extract and the acetone washes were separately concentrated on a rotary film evaporator at 35 °C, and the concentrated extracts were analyzed by TLC in solvent systems a and b.

The major radioactive component in the washes of rice plants was isolated for mass spectrometry in a similar manner to that described for the radioactive soil metabolites.

RESULTS

Analysis of Soil Samples. Amounts of radioactivity measured in soil samples at intervals during the study are shown in Table I. The distribution of this radioactivity between supernatant water, solvent extracts, and insoluble residue is also shown. Total quantities of radioactivity in soil samples were similar (90 ± 5% SD), within the limits of experimental error, up to 16 weeks after application but declined to a mean value of 64% at 32 weeks, indicating some loss of radioactivity by volatilization during prolonged storage. The amounts of radioactivity in supernatant water and solvent extracts decreased with time.

In a separate experiment, a mean of 9% of the applied radioactivity was released as volatile radioactivity from soil in flasks sealed for 32 weeks. Most of this was trapped as $^{14}CO_2$ before passage of the flask contents through the catalytic furnace. This result could represent a low value for volatile radioactivity production as the oxygen content of the flasks was not replenished during the experiment, it being considered that anaerobic metabolism would be more important in flooded soil. The lower recovery (64%) of radioactivity from the 32-week stored soils in open flasks could be due to loss of radioactivity by volatilization.

The nature of the radioactivity in supernatant water and solvent extracts of soil was investigated by TLC. Two solvent systems were used separately to provide a complete profile of radioactive components. Solvent system b provided the best separation of the major radioactive components, and the results from this system are shown in Table II.

Unchanged techlofthalam was detected in significant quantities up to 16 weeks after application but was present in only small amounts in both supernatant water and the organic extracts at 32 weeks. Two major radioactive metabolites (components 1 and 2, Table II) were separated. These components were isolated from a high level treated soil, stored for 48 weeks, and identified, by mass spectrometry, as isomers resulting from the replacement of one chlorine atom from the phthalamic acid moiety by hydrogen. The TLC results suggested that one of these two isomers (component 1, Table II) was not produced in significant quantities before 16 weeks. This may indicate that there is a lag phase and the degradation increases in acclimated soil. However, GC–MS analysis of the major radioactive band isolated by preparative TLC of extracts from soils incubated for 4 weeks with [^{14}C]techlofthalam at the higher application rate showed that the TLC separation of these very similar molecules was not complete. This major band consisted mainly of unchanged techlofthalam but also contained a small contribution from a monodechlorinated product. It was not possible to precisely quantitate this contribution as some decarboxylation of both compounds took place during the gas chromatography and the monodechlorinated compound was not well separated from the decarboxylation product of techlofthalam. As a result of this, the proportions given in Table II may only give an indication of the amounts present. There are, of course, four possible isomers of the monodechlorinated product, and it is possible that all were present. Two further minor radioactive components were resolved by solvent system b, but these were not identified.

The imide of techlofthalam appeared to be unstable in solvent system b but was well separated in solvent system a. Results from this system showed that the imide was a minor metabolite in soil, accounting for a maximum of 2.5% of the applied radioactivity at 16 weeks after application. The imide was mainly present in solvent extracts of soil rather than in the supernatant water.

Mass Spectrometry of Soil Metabolites. The mass spectra of techlofthalam and its dechlorinated metabolites
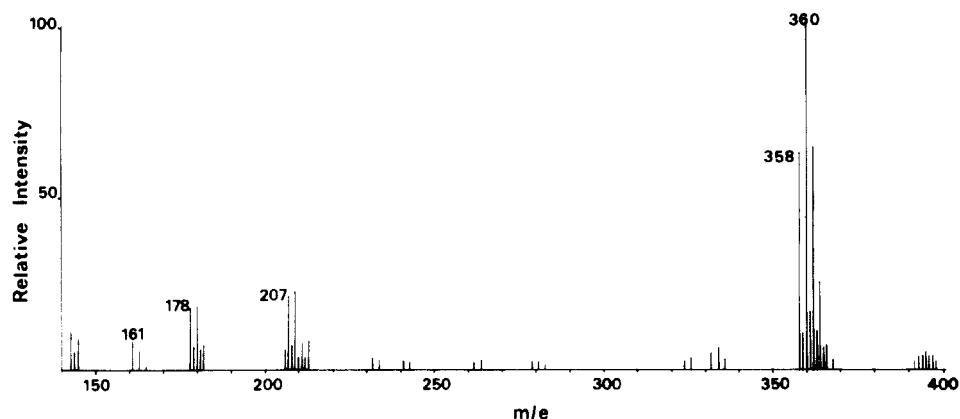
Figure 1. Mass spectrum of a monodechlorinated degradation product isolated from soil.

Table III. Quantities of Radioactivity in the Acetone Washings and Extracts and Insoluble Residues of Treated Rice Leaves after Application of [^{14}C]Techlofthalam[a]

time after application, days	wash	extracts	residue
1	87.0	7.3	5.7
	85.7	8.8	5.5
3	92.4	3.6	4.0
	94.6	2.1	3.3
7	90.2	6.4	3.4
	91.7	5.2	3.1
15	96.3	1.7	2.0
	89.6	5.7	4.7
30	91.4	3.6	5.0
	88.8	5.8	5.4

[a] Results are expressed as percent total recovered radioactivity and are given for duplicate samples at each time.

Table IV. Proportions[a] of Radioactive Components in the Acetone Washings of Rice Leaves

time after application, days	radioactive component no. (approx. R_f)[b]		
	1 (0.45)[c]	2 (0.93)	others
1	94.8	2.9	2.3
7	88.7	9.1	2.2
15	84.1	13.3	2.6
30	79.1	17.1	3.8

[a] Results are expressed as percent radioactivity in each wash. [b] Solvent system a. [c] Corresponds to techlofthalam.

showed characteristic fragmentation patterns. No molecular ions were observed but low-intensity M – H_2O ions and high-intensity ions resulting from further loss of chlorine were seen. Other fragmentations which occurred were decarboxylation and amide bond cleavage. Relative intensities of these ions varied with the temperature of the insertion probe.

The mass spectrum (probe temperature 100 °C) of one of the monodechlorinated metabolites is shown in Figure 1. In this spectrum, amide bond cleavage resulted in the group of ions at m/e 161, etc. (with peak ratios characteristic of two chlorines) from the dichloroaniline part of the molecule, showing that the degradative dechlorination had occurred in the phthalamic acid part of the molecule. This was confirmed by the presence of fragments derived from that part of the molecule at m/e 207, resulting from amide bond cleavage and decarboxylation, and at m/e 178, resulting from further loss of CO, which both showed peak ratios characteristic of three chlorine atoms. The base peak in this spectrum (m/e 358) was due to loss of water and chlorine from the parent molecule, but no molecular ion was observed.

Analysis of Rice Plants. The distribution of radioactivity in treated rice leaves between washes, extracts, and insoluble residues is shown in Table III. Very little translocation (<2% applied) of radioactivity to untreated parts of plant occurred. Most of the radioactivity on the treated leaves was removed by washing with acetone, although this does not necessarily indicate that all the radioactivity remained on the leaf surface. TLC in solvent system a (Table IV) of these washes showed that an increasing proportion of radioactivity was associated with the imide of techlofthalam, although unchanged tech-

lofthalam was the major component at all times. TLC in solvent system b did not reveal any further radioactive components. The identity of the unchanged techlofthalam was confirmed by mass spectrometry after isolation of the major radioactive component.

Radioactivity in extracts of treated rice leaves was partitioned between water and chloroform. About 90% of the radioactivity was present in the chloroform phase. TLC (solvent systems a and b) showed that radioactivity in the chloroform phase was mainly associated with techlofthalam and its imide up to day 15 but that the day 30 sample contained several other unidentified radioactive metabolites and very little techlofthalam. From the above results, the total concentrations of techlofthalam and its imide in treated rice leaves at 30 days after treatment (including the contribution from the acetone wash) can be calculated to be about 39 and 9 μg/g, respectively.

DISCUSSION

The results of the soil study showed that [^{14}C]techlofthalam was slowly degraded under simulated paddy field conditions. The principal degradation pathway appeared to be reductive dechlorination, although during the time course of the study, no products were identified in which more than one chlorine had been replaced.

No metabolites were detected resulting from hydrolysis of the amide bond in the molecule, although it is possible that the hydrolysis products, particularly dichloroaniline, would have been strongly bound to soil and not extracted by the solvents used. The existence of further degradation pathways was indicated by the detection of $^{14}CO_2$ of which the most likely source would seem to be from the radiolabel in the carboxylic acid group, which would then yield a metabolite with a specific activity lower than that of techlofthalam and possibly less polar. Minor less polar metabolites were detected by TLC but were not identified.

Reductive dechlorination has also been shown to be an important degradative pathway for certain other poly-

chlorinated aromatic compounds in paddy soil. Pentachlorophenol was reported to be rapidly degraded in laboratory-stored paddy soil with the formation of all three possible isomeric tetrachlorophenols, 2,4,5- and 2,3,5-trichlorophenols, 3,4- and 3,5-dichlorophenols, and 3-chlorophenol (Ide et al., 1972). In paddy field soil, residues of nitrofen (2,4-dichloro-4'-nitrodiphenyl ether) were detected in fields treated 10 months previously with 4'-nitro-2,4,6-trichlorodiphenyl ether (Yamada, 1976). In view of the results obtained with pentachlorophenol, it is perhaps surprising that significant further dechlorination of techlofthalam was not observed. However, it has been shown (Alexander and Aleem, 1961) that the rate of decomposition of various chlorinated phenols and phenoxyalkanoic acids by soil microbial cultures is very dependent on the positioning of chlorine substituents on the aromatic nucleus.

Most of the radioactivity applied to the leaves of rice plants could be recovered by washing with acetone for samples collected up to 30 days after the application. Techlofthalam was the major component in these washes, but the proportion of techlofthalam imide increased to about 20% of the radioactivity at 30 days. The same two components were also detected in solvent extracts of the

same leaves sampled up to 15 days, although by 30 days techlofthalam was only a minor component. Formation of the imide appears to be the major initial transformation which could be a chemical process on the leaf surface or an enzymic reaction within the leaf. However, at least some penetration of the applied techlofthalam probably occurs since this compound was detected in the solvent extracts of washed leaves.

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Biphenyl Formation in the Photolysis of 3-(4-Chlorophenyl)-1,1-dimethylurea (Monuron) in Aqueous Solution

Fred S. Tanaka,* Ronald G. Wien, and Barry L. Hoffer

In the photolysis of dilute aqueous solutions of monuron, a photoproduct with a mass spectral molecular ion at m/e 360 was isolated and partially characterized. Initial data suggested that the unknown product was a substituted diphenylamine, and this material was apparently being formed by photocoupling of two monuron molecules with concomitant elimination of hydrogen chloride. Upon further examination, however, the photoproduct was characterized as a substituted biphenyl compound. After hydrolysis and acetylation of the unknown, high-performance liquid chromatography revealed that the photoproduct was a mixture of two isomeric compounds. When synthetic and spectroscopic methods were employed, the isomeric biphenyl photoproducts were identified as the 2-chloro-4',5-bis(N',N'-dimethylureido)biphenyl and the 5-chloro-2,4'-bis(N',N'-dimethylureido)biphenyl. The 5-chloro isomer represented 92% of the isomeric mixture, and the 2-chloro isomer represented the remaining 8%.

During the investigation of the photolysis of monuron in dilute aqueous solution, a photoproduct with a molecular mass equivalent to the coupling of two monuron molecules minus the mass of hydrogen chloride was isolated and partially characterized (Tanaka et al., 1977). This compound was the second most abundant photoproduct isolated and was observed in 2% yield after a 45-min exposure period in a Rayonet reactor equipped with sunlight lamps. During this exposure period, about 29% of the monuron was decomposed; therefore, approximately 7% of the decomposed monuron was transformed into this unknown photoproduct. The identity of the unknown photoproduct was of considerable interest because Rosen and Strusz (1968) detected a photoproduct of similar nature from natural sunlight photolysis of metrobromuron.

Since hydrogen chloride was the only product eliminated from the coupling of two monuron molecules, the results suggested that a substituted diphenylamine was probably being produced. There was some question, however, as to the position of aromatic coupling (Tanaka et al., 1977). Consequently, further study was necessary to determine complete identification of the coupled photoproduct.

EXPERIMENTAL METHODS

Materials and Equipment. The 2-chloro-5-nitroaniline and 5-chloro-2-nitrobenzoic acid were purchased from Aldrich Chemical Co. The 1,5-naphthalenedisulfonic acid (sodium salt) was obtained from Eastman Kodak Co. [*ring*-^{14}C]Monuron was prepared in the laboratory (Tanaka, 1970).

Sample preparation, photolysis with the Rayonet photoreactor, and photoproduct isolation were conducted as previously described (Tanaka et al., 1977). Infrared (IR) spectra were taken on a Perkin-Elmer Model 399 spectrophotometer equipped with the Model 3500 data handling station. Mass spectra were obtained on a Varian

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