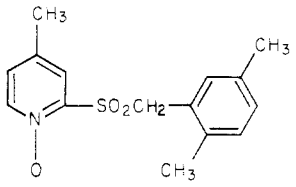
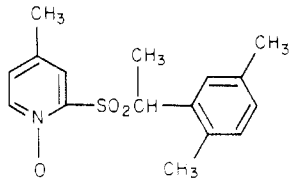
compounds with substituents only in the 3-, 4-, or 5-position. Within each of these three groupings, the activity was surprisingly similar regardless of the electronic and hydrophobic character of the substituents. This, along with the data on the α-benzyl substituents, strongly suggests the desirability of some steric congestion in the region between the two rings. It also suggests a certain insensitivity toward overall hydrophobic effects on the molecule.

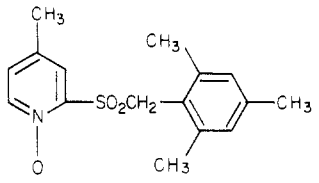
PGR Activity. The compounds **12–14** showed turf



12



13



14

retardation activity that was superior to that of both the standard, Embark, and the analogous compounds without a 4-methyl substituent on the pyridine ring, from the standpoint of both grass regrowth and phytotoxicity to the grasses.

Registry No. 1 (X = 3-Me, R = H, Z = 2,5-Me_2), 81167-56-8; 1 (X = 4-*t*-Bu, R = H, Z = 2,5-Me_2), 81167-62-6; 1 (X = 4-Ph, R = H, Z = 2,5-Me_2), 81167-59-1; 1 (X = 4-Cl, R = H, Z = 2,5-Me_2), 81167-77-3; 1 (X = 5-Br, R = H, Z = 2,5-Me_2), 81167-73-9; 1 (X = 4-CN, R = H, Z = 2,5-Me_2), 81167-64-8; 1 (X = 5-NO_2, R = H, Z = 2,5-Me_2), 88496-43-9; 1 (X = 5-Me, R = H, Z = 2,5-Me_2), 81167-72-8; 1 (X = 6-Me, R = H, Z = 2,5-Me_2), 81167-66-0; 1 (X = 3,4-Me_2, R = H, Z = 2,5-Me_2), 81167-76-2; 1 (X = 4,5-Me_2, R = H, Z = 2,5-Me_2), 81167-75-1; 1 (X = 4-Me, R = *i*-Pr, Z = 2,5-Me_2), 88496-44-0; 1 (X = 4-Me, R = *n*-hexyl, Z = 2,5-Me_2), 88496-45-1; 1 (X = 4-Me, R = Ph, Z = 2,5-Me_2), 88496-46-2; 1 (X = 4-Me, R = H, Z = 2,6-Cl_2, 81167-84-2; 1 (X = 4-Me, R = H, Z = 2-Me), 81167-78-4; 1 (X = 4-Me, R = H, Z = 4-*t*-Bu), 81167-80-8; 1 (X = 4-Me, R = H, Z = 4-F), 88496-47-3; 1 (X = 4-Me, R = H, Z = 4-Ph), 81167-81-9; 1 (X = 4-Me, R = H, Z = 4-NO_2), 81167-87-5; 1 (X = 4-Me, R = H, Z = 3-CN), 81167-85-3; 1 (X = 4-Me, R = H, Z = 3-CF_3), 81167-82-0; **2** (X = 4-Me), 4926-28-7; **2** (X = 3-Me), 3430-17-9; **3** (R = H, Z = 2,5-Me_2), 22182-98-5; **4** (X = 4-Me, R = H, Z = 2,5-Me_2), 81167-55-7; **4** (X = 4-Me, R = Me, Z = 2,5-Me_2), 88496-48-4; **4** (X = 4-Me, R = H, Z = 2,4,6-Me_3), 88496-51-9; **5** (X = 3-Me, R = H, Z = 2,5-Me_2), 81167-57-9; **6** (R = Me), 81167-67-1; **7**, 60263-80-1; **8**, 88496-50-8; **9**, 88496-49-5; **10**, 81167-79-5; **12**, 81167-93-3; **13**, 81167-91-1; **14**, 81167-88-6; MCPBA, 937-14-4; 2-[(2,5-dimethylbenzyl)-sulfinyl]pyridine 1-oxide, 60264-17-7; 2-[(2,5-dimethylbenzyl)-sulfinyl]-4-methylpyridine 1-oxide, 81167-68-2; 2-[(2,5-dimethylbenzyl)sulfinyl]-3-methylpyridine 1-oxide, 81167-92-2; 2-mercapto-4-methylpyridine, 18368-65-5; 4-methylpyridine 1-oxide, 1003-67-4; 2-bromo-3-methylpyridine 1-oxide, 19230-57-0.

LITERATURE CITED

Abramovitch, R. A.; Knaus, E. E. *J. Heterocyl. Chem.* **1975**, *12*, 683.

Plant, H. L.; Bell, A. R. U.S. Patent 3 960 542, 1976.

Received for review April 7, 1983. Accepted December 1, 1983.

Photodecomposition of Propachlor

Miriam Rejtö, Sarina Saltzman, and Aureliu J. Acher*

The photolysis of solutions of propachlor (I) was investigated. Photolysis carried out under UV light (5 h) led to about 80% decomposition of I. The three photodegradation products isolated were *N*-isopropyloxindole (II), *N*-isopropyl-3-hydroxyoxindole (III), and a spiro compound (IV). Photolysis performed under visible light (12 h) of the solution of I containing riboflavin led to the almost complete photodegradation of the title compound. From the irradiated solutions, only minute amounts of one photodegradation product were isolated and identified: *m*-hydroxypropachlor (V). The chemical structures of the photodegradation products were determined by spectroscopic methods. The structures of II and V were also confirmed by comparison with those of the authentic samples prepared by chemical methods. The photodegradation products in the reaction mixture from visible light experiments were checked for phytotoxicity and found to be nontoxic to the test plants.

Propachlor (2-chloro-*N*-isopropylacetanilide, I) is a preemergence herbicide effective against annual grasses and certain broad-leaved weeds (Martin, 1972). It was selected as a representative of the anilide herbicide group for photodecomposition studies aimed at finding a photochemical method of detoxification of water from organic pollutants. Such studies have already been carried out with uracil (Acher and Dunkelblum, 1979; Acher and Saltzman, 1980; Acher et al. 1981; Saltzman et al., 1982) and with *s*-triazine herbicides (Rejtö et al., 1983).

Herbicides from the anilide group are known as general growth inhibitors of young seedlings or inhibitors of root growth. Studies of the specific mode of action of I showed that it causes a reduction in cell elongation and cell division rate, by inhibiting protein synthesis in root tips (Ashton and Crafts, 1973). The degradation of I in corn and soybeans has been reported (Jaworski, 1969), but the structure

Division of Soil Residues Chemistry, Institute of Soils and Water, ARO, The Volcani Center, Bet Dagan 50-250, Israel.

0021-8561/84/1432-0226$01.50/0

of the metabolite has not been defined. It was suggested that the chlorine atom of I has been displaced by a nucleophilic substrate in the plants.

Anilide compounds were found to rearrange under UV light (Elad et al., 1965) and anilide herbicides might be expected to behave similarly (Crosby and Ming-Yu, 1969). However, virtually nothing has been reported on the photodecomposition of this group of herbicides.

The goal of this work was to study the photolysis of I under visible and UV light at different reaction conditions, to isolate and identify the photoreaction products, and to check for their phytotoxic properties.

EXPERIMENTAL SECTION

Materials. *Propachlor (I)* (provided by Agan, Ltd., Israel) was crystallized from 2-propanol–water, mp 71–72 °C [lit. mp 67–76 °C; water solubility at 20 °C, 0.07% (Martin, 1972)].

N-Isopropyloxindole (1,2-dihydro-1-isopropyl-2*H*-indol-2-one, II) was synthesized by cyclization of I with anhydrous $AlCl_3$ (Stolle, 1930). This reaction gave, beside II, the N-dealkylated oxindole, mp 125–126 °C [lit. mp 127 °C (Harris, 1965)].

m-Hydroxy-2-chloro-N-isopropylacetanilide (V). The methyl ether derivative was synthesized from *m*-anisidine by a method described by Walker et al. (1970). The cleavage of the methyl ether with BBr_3 (Benton and Dillon, 1942) afforded V.

The sensitizers riboflavin (RF) (BDH, H21632 Q) and methylene blue (MB) (BDH, H21632 Q) were used as freshly prepared water (deionized) solutions (200 mg L^{-1} for RF and 100 mg L^{-1} for MB) or dissolved directly into the herbicide solutions before irradation.

The aqueous solutions tested by bioassay were different concentrations of I (0.5, 1, 5, 10 mg L^{-1}), and the visible light irradiated solution (initial concentration 40 mg L^{-1} RF; I, 0.3 mol/mol, pH 4). The irradiated reaction mixture still contained 0.7 mg L^{-1} I after 10 h of irradiation; its pH was adjusted to 6.5 before use. This solution was checked as such (A) and after dilution 1:4 (B).

The test plants used were oat (*Avena sativa*), sorghum (*Sorghum bicolor*), and tomatoes (*Solanum lycopersicum*).

Methods. The gas chromatograph used was a Tracor No. 506 instrument equipped with a Tracor No. 702 NP detector and a glass column (1.2 m × 2 mm i.d.) filled with 3% OV-17 on Gas-Chrom Q, 80–100 mesh. The gas carrier was dry N_2 (15 mL/min). The chromatograms were run isothermally at an oven temperature of 190 °C. Compound V was silylated with BSTFA [bis(trimethylsilyl)trifluoroacetamide] before GC analysis.

Chemical ionization (CI) mass spectra (70 eV) were recorded on a Du Pont No. 490 B, low-resolution mass spectrometer, equipped with a dual EI/CI ion source (source temperature, 190 °C; sample temperature, 200 °C). High-resolution mass spectra were recorded on a MS-Varian MAT No. 731. The IR spectra were run on a Perkin-Elmer No. 257 instrument in KBr pellets. The H NMR spectra were run on a Varian FT-80A spectrometer (80 MHz) and the ^{13}C NMR spectra were run on a Bruker WH-270 spectrometer with $CDCl_3$ (unless otherwise stated), and all spectra are reported in δ from Me_4Si (internal standard). A Varian UV–vis spectrophotometer, Techtron No. 635, was used for spectrophotometric measurements. The light intensity in the 400–700-nm range was measured by a quantum sensor (Lambda Instrument Corp., Nebraska) connected to a digital integrator (Type TS 100A). The melting points were determined by using a Fisher digital melting point analyzer, No. 355, and were not corrected.

Column chromatography was performed on silica gel (230–400 mesh, Merck art. 9385) using a rapid chromatographic technique (Still et al., 1978). Columns were eluted with ethyl acetate (EA)–methylene chloride (MC), 2:98, for separation of the photoproducts from the mixture irradiated with UV light (unless stated otherwise) and with MC–EA, 10:1, for the mixture irradiated with visible light. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (60 F 254, Merck art. 5549) and developed in MC–EA, 9:1. The spots were revealed by UV light or by iodine vapors.

Photodecomposition Procedure. *Using UV Light.* The photoreactions with UV light were carried out in an open dish (250 mL) equipped with a magnetic stirrer. The UV source (254 nm) consisted of four lamps (57413P/40, TUV 30W, Philips, Holland) mounted above the dish. To facilitate the isolation of the photodegradation products from the irradiated solutions, the concentration of I was increased up to 1.0% by using ethanol–water (80:20) solutions. An amount of 200 mL of solution was exposed to UV light while stirring. The photodecomposition progress was followed by TLC. After irradiation, the solvent was removed and the dry residue was submitted to column chromatography.

Using Visible Light. The photoreactions with visible light were carried out in graduated Pyrex cylinders (500 mL), with direct outdoors solar irradiation (from May to Sept 1982; altitude 100 m, latitude 32° N, longitude 34°50′ E), or in a laboratory photoreactor equipped with a 400-W visible light lamp (Osram-Power Star-HQI, West Germany) mounted vertically and cooled by an air blower. The cylinders containing the solutions were arranged in a circle around the lamp and about 3-cm distance from it.

Aqueous solutions of I (0.5 g, 1 L) and RF (125 mg) adjusted to pH 4 (0.01 N HCl) were exposed to visible light in the photoreactor (~2400 μEinsteins m^{-2} s^{-1}). During the irradiation, air (water washed) or argon (pyrogallol washed) was flushed through an 0.1-mL pipet at the bottom of the solutions. The temperature of the solutions reached about 40 °C.

The irradiations were followed by continuous sampling of the irradiated solutions and the injection of their ethyl acetate extracts into the GC. The extracts were prepared by shaking the sample (1 mL) with ammonium sulfate (0.5 g) and EA (5 mL) in a stoppered test tube for about 30 s. The upper layer was further diluted with the same solvent to a final concentration of only a few milligrams per liter. This diluate was injected into the GC column (2 μL).

After irradiation the solution was lyophilized and the dry residue obtained was submitted to column chromatography.

Blank experiments irradiated without sensitizer or kept with sensitizer in the dark were carried out with each series of all above experiments.

Bioassay Procedure. Seedlings (2-day-old oat germinated on filter paper and 7- and 11-day-old sorghum and tomatoes, respectively, germinated in vermiculite) were transferred to glass tubes (10 mL) with the root immersed in the test solutions. The experiment was carried out in a growth chamber, at constant temperature (25 °C) and normal light conditions (16-h light, 8-h dark), and was run in 10 repetitions. Visual estimation of plant development showed that differences in the root system between seedlings grown in a solution of I and the control appeared as early as after 4 days. Therefore, the assessments were made at this early stage, which also avoids the interference of eventual injury caused by the lack of nutrient elements

Scheme I. Main Photodegradation Products of Propachlor (I)

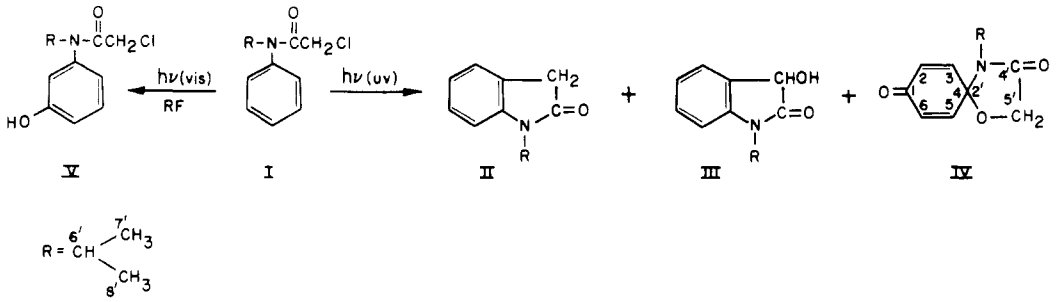


Table I. High-Resolution MS, Significant Peaks, and Major Fragmentation of Photodecomposition Products of I

product	mass found	% abundancy	composition	
II	175.0995	49.52	$C_{11}H_{13}NO$	M^+
	160.0796	34.09	$C_{10}H_{10}NO$	$M^+ - CH_3$
	133.0539	44.73	C_8H_7NO	$M^+ - C_3H_6$
	132.0809	100.00	$C_9H_{10}N$	$M^+ - C_2H_3O$
III	191.0899	30.94	$C_{11}H_{13}NO_2$	M^+
	163.0960	24.13	$C_{10}H_{13}NO$	$M^+ - CO$
	162.0929	78.84	$C_{10}H_{12}NO$	$M^+ - CHO$
	120.0434	100.00	C_7H_6NO	$M^+ - C_4H_7O$
IV	207.0865	89.89	$C_{11}H_{13}NO_3$	M^+
	192.0683	20.45	$C_{10}H_{10}NO_3$	$M^+ - CH_3$
	179.0923	5.17	$C_{10}H_{13}NO_2$	$M^+ - CO$
	165.0403	84.52	$C_8H_7NO_3$	$M^+ - C_3H_6$
	134.0585	96.94	C_8H_8NO	$M^+ - CH_3 - C_2H_2O_2$
V	227.066	57.36	$C_{11}H_{14}NO_2Cl$[a]	M^+
	212.0409	21.06	$C_{10}H_{11}NO_2Cl$[a]	$M^+ - CH_3$
	192.1005	54.67	$C_{11}H_{14}NO_2$	$M^+ - Cl$
	185.0194	30.88	$C_8H_8NO_2Cl$[a]	$M^+ - C_3H_6$
	136.0586	100.00	$C_8H_8O_2$	$M^+ - C_3H_6NCl$

[a] Another M^+ peak, corresponding to the ^{37}Cl isotope, was present.

and root aeration in the solution tested. The parameters used to evaluate the response of the plants were visual assessments of injury symptoms, root and shoot elongation, and the dry weight. The results are mean values eventually expressed as percent of the control (seedlings grown under the same conditions, in distilled water).

RESULTS

Identification of the Photodecomposition Products of I, Irradiated with UV Light. Irradiation of ethanolic solution of I with UV light (5 h) resulted in about 80% decomposition (based on recovered I) and gave a complex mixture of photoproducts, the composition of which was dependent on the irradiation time. Longer irradiation times caused further decomposition of I and its photoproducts. Replacement of air by argon, using special quartz dishes, eliminated the formation of compound IV and III and significantly decreased the formation of II.

Column chromatography of the residue of the UV-irradiated ethanolic solutions separated unreacted I (R_f = 0.55) and three degradation products II (R_f = 0.40), III (R_f = 0.21), and IV (R_f = 0.28) in low yields (Scheme I). No differences were observed among the identities of photoreaction products formed in ethanolic solutions and those formed in water solutions.

1,3-Dihydro-1-isopropyl-2H-indol-2-one (II). Chromatographically pure II was obtained in about 5% yield by column chromatography of a mixture of I and II by using MC as the eluent. This mixture of I and II was obtained from the irradiated reaction mixture residue by a rapid column chromatography technique (Still et al., 1978). White needles of II, mp 52–53 °C, were obtained by crystallization from *n*-hexane. Its mass spectrum showed a molecular ion with *m/e* 175 corresponding to $C_{11}H_{13}NO$, indicating elimination of an HCl molecule from I (Table I). The H NMR spectrum indicated the presence of an isopropyl group (δ 1.47, d, J = 7 Hz, 6 H, and δ 4.67, septet, 1 H), a methylene group (δ 3.49, s, 2 H) and four aromatic protons (δ 7.20, m); the IR spectrum showed the carboxyl band at 1715 cm^{-1}. Compound II was found to be identical in all aspects with an authentic sample of *N*-isopropyl oxindole prepared by a chemical method (Stolle, 1930).

UV photolysis of ethanolic solutions of II produced neither III nor IV but resulted in unidentified products in small amounts that were not investigated further.

1,3-Dihydro-1-isopropyl-3-hydroxy-2H-indol-2-one (III). Crystallization of crude III, obtained by column chromatography of the irradiated mixture residue, in about 5% yield, gave crystals of III, mp 88–90 °C (*n*-hexane). The mass spectrum showed a molecular ion with *m/e* 191 corresponding to $C_{11}H_{13}NO_2$, indicating the elimination of an HCl molecule and the addition of one oxygen atom (Table I). The H NMR spectrum showed the presence of two prochiral CH_3 groups of the isopropyl group (δ 1.07 and 1.08, dd, J = 6.8 Hz, 6 H), one hydroxyl group (δ 3.45, d, J = 12 Hz, 1 H), one C*H*OH group (δ 4.68, d, J = 12 Hz, 1 H), one $CH(CH_3)_2$ proton (4.88, septet, 1 H), and four aromatic protons (δ 7.42, m, 4 H). Addition of D_2O led to the disappearance of the doublet at δ 3.45 and conversion of the doublet at δ 4.68 to a singlet.

Treatment of III with acetic anhydride and pyridine gave the corresponding acetate, the H NMR spectrum of which showed the disappearance of the hydroxyl proton, the appearance of an acetyl group (δ 2.07, s, 3 H), and a large shift of the proton α to the acetyl group (δ 6.45, s, 1 H).

Spiro[2,5-cyclohexadien-1-one-4,2′-3′-isopropyl-oxazolidin-4′-one] (IV). Crystallization of crude IV, obtained by column chromatgraphy of the irradiated mixture residue, in about 3% yield, gave pale yellow needles, mp

118–120 °C (*n*-hexane). The mass spectrum of IV indicated the loss of chlorine and a hydrogen atom and the addition of two oxygen atoms as compared to the parent compound, structure I. The molecular ion at *m/e* 207 corresponds to $C_{11}H_{13}NO_3$ and the major fragmentation supports the structure proposed (Table I). The H NMR spectrum showed the presence of an isopropyl group (δ 1.38, d, J = 6.9 Hz, 6 H, and δ 3.5, septet, 1 H), a methylene group (δ 4.34, s, 2 H), and four vinylic hydrogens (δ 6.31, d, J = 10.2 Hz, 2 H, and δ 6.68, d, J = 10.2 Hz, 2 H). The shape of the latter signals resembles an AA'XX' pattern, characteristic for para-substituted aromatic rings; however, the coupling constant, 10.2 Hz, indicates splitting between cis double bond protons rather than splitting between aromatic protons. The ^{13}C NMR spectrum showed three signals at δ 184.0 (C-1, s), 144.3 (C-3 and C-5, d), and 130.7 (C-2 and C-6, d) that are characteristic for 2,5-cyclohexadien-1-one derivatives [δ 184.1, 144.4 and 130.8, respectively (Gramlich, 1979)]. The signal corresponding to the quaternary carbon, C-4, linked to C-3, C-5, oxygen, and nitrogen atoms, appears at δ 88.0, s [compared to δ 85.7, s, of the signal of a similar substituted quaternary carbon, C-5, observed in a hydantoin derivative (Acher and Dunkelblum, 1979)]. Other signals appear at δ 169.4 (C'-4, s), 67.3 (C'-5, t), 45.8 (C'-7 and C'-8, d), and 20.8 (C'-6, q).

The IR spectrum showed the carbonyl band of the five-membered ring lactam at 1715 cm^{-1}, the carbonyl of quinone at 1675 cm^{-1} and the conjugated double bond at 1635 cm^{-1}.

Identification of the Photodecomposition Products of I, Irradiated with Visible Light. Aqueous solutions of I were found to be photostable upon exposure to visible light. However, addition of RF to these solutions was very efficient in sensitizing the photodecomposition reaction; the dye, MB, did not have a significant sensitizing effect; replacement of air with argon eliminated the sensitized photodecomposition reaction.

The decomposition rate of I was found to depend on the initial pH of the reaction mixture and on the molecular ratio RF to I. The most suitable working conditions used were pH 3–4 (the fastest decomposition) and a ratio of RF to I of ~0.1.

Irradiation of the aqueous solution of I (2.8×10^{-3} M) in the presence of RF (3.5×10^{-4} M) at pH 4 for 9 h resulted in 60% decomposition of I. TLC analysis of the irradiated solution showed, in addition to the spot corresponding to I, a weak spot corresponding to V (R_f = 0.20), visualized in iodine. Further irradiation of this solution (12 h) resulted in the complete decomposition of both I and V. Column chromatography of the dry residue after lyophilization of the reaction mixture separated unreacted I and its meta-hydroxylated derivative V (3% yield) (Scheme I).

m-Hydroxy-2-chloro-N-isopropylacetanilide (*V*). The crude V, obtained from column chromatography, was crystallized from ethyl acetate, mp 217–218 °C. The MS gave a molecular ion at *m/e* 227, which indicated addition of an oxygen atom to I (Table I). The H NMR (Me_2SO) spectrum showed the presence of an isopropyl group (δ 1.00, d, J = 6.7 Hz, 6 H, and δ 4.70, septet, 1 H), a methylene group (δ 3.82, s, 2 H), and four aromatic protons. Three aromatic protons overlap near δ 6.75, while the fourth proton, meta to the substituents, resonates at a lower field (δ 7.25) as a di ortho triplet. The IR spectrum indicated the presence of an OH group (3230 cm^{-1}) and a meta-disubstituted benzene ring (720, 780 cm^{-1}). Compound V was found to be identical with *m*-hydroxy 2-chloro-*N*-isopropylacetanilide prepared by chemical methods (Walker et al., 1970; Benton and Dillon, 1942).

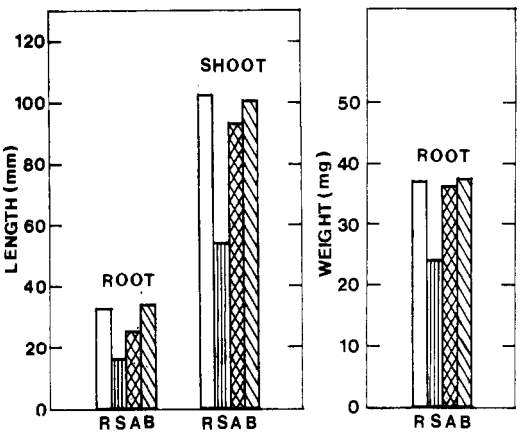


Figure 1. Effect of photodegradation reaction mixtures on oat seedlings. R = distilled water; S = 10 mg L^{-1} I; A = 40 mg L^{-1} I irradiated; B = the same as A, diluted 1:4.

Irradiation of aqueous solution of V (180 mg L^{-1} V, 20 mg L^{-1} RF, pH 4) for 15 min resulted in its almost complete decomposition (~95%) but no degradation products could be detected.

Phytotoxicity Test. The application of I to the roots of young barley seedlings decreased the accumulation of fresh and dry matter and reduced root and shoot elongation (Klendgen, 1980). On the basis of this and previous information, a study was made of the effect of solutions and irradiated reaction mixture of I on the early seedling growth of susceptible plants.

Dose–response curves considering all the parameters measured showed that the order of sensitivity of the test plants to I was oat > sorghum > tomatoes. Oat, which was the most sensitive (even at 0.5 mg L^{-1}) and had an almost quantitative response to I, was selected to be used for the toxicity test of irradiated solutions. Figure 1 shows the effect of irradiated reaction mixture of I (A and B) on root and shoot length and root weight as compared with the same effects of a solution of 10 mg L^{-1} of I (S) and distilled water (R). The nonlethal effect of S may be attributed to the very young age of the oat seedlings.

The irradiated mixture A, which initially contained 40 mg L^{-1} of I, had a slight growth-inhibiting effect. It decreased root elongation by 21%, as compared with a 49% decrease caused by 10 mg L^{-1} I. The decrease in shoot elongation was 9%, and the decrease in root weight was only 2%, whereas the effect of the nonirradiated solution was 47% and 35%, respectively. The diluted (1:4) irradiated mixture, B, did not affect the development of the young oat seedlings; the values obtained for all the parameters measured were similar to those for the control.

DISCUSSION

The photodecomposition of I was achieved by either UV or visible light. However, the photodegradation pathway was completely different and products formed under UV irradiation (II, III, IV) were not detected in RF-sensitized solutions exposed to visible light and vice versa.

The necessary presence of O_2 or RF (under visible light) in the photoreaction mixtures was proven by carrying out blank experiments (under argon or without RF), which gave no reaction products III, IV and V, and only traces of the product II.

The low yields of the degradation compounds might be explained by their lability under the photoreaction conditions, which obviate their accumulation and cause their rapid disappearance when the parent compound is depleted.

Although the mechanism of formation of the photodegradation products is beyond the aim of this study, it seems very plausible that the photodecomposition of I under UV light involves, as a first step, a homolytic C–Cl cleavage in I with subsequent reaction of the radical formed either with benzene ring, leading to oxindole derivatives (II and III) or with molecular oxygen leading eventually to a spiro derivative (V) (Scheme I).

Since N-aryl amides of carboxylic acids are known to cleave and rearrange themselves under UV irradiation [the photo Fries rearrangement, (Elad et al., 1965)], the possibility of such a reaction was taken into consideration when the structure of II was established. However, the data from H NMR and mass spectra were not unequivocal and therefore the assignment of the structure of II was done by comparing it with an authentic sample of *N*-isopropyloxindole (Stolle, 1930). The identity of the compounds ruled out the possibility of a rearrangment reaction of I prior to cyclization.

The assignment of the structure of IV was obtained by combining spectra data from ^{13}C NMR, which showed signals characteristic for 2,5-cyclohexadien-1-one derivatives (Gramlich, 1979), with H NMR, which showed signals of vinylic hydrogens with a coupling constant (J = 10.2 Hz) specific to a cis double bond. The changes in the chemical shifts (from I to IV) of the methyne (from δ 4.95 to 3.5) and of methylene protons (from δ 3.70 to 4.34) fit with the formation of the five-membered lactam ring. Also, the major fragmentation [CO, $CH(CH_3)_2$, CH_3–$C_2H_2O_2$] occurring at high-resolution MS (Table I) supports the structure IV.

The data accumulated from the irradiation of the sensitized solution with visible light suggested that the primary step in the photodecomposition of I is the hydroxylation of the aromatic ring leading to the phenol derivative V. The assignment of the structure of V was also done, beside the spectrometrical methods, by its comparison with an authentic sample of *m*-hydroxy-2-chloro-*N*-isopropylacetanilide prepared by chemical methods (Walker et al., 1970; Benton and Dillon, 1942).

Since the practical goal of the photodegradation studies of herbicides is the detoxification of polluted water in order to enable its reutilization in crop irrigation, the characterization of the phytotoxicity of visible light irradiated herbicide solutions was necessary. The phytotoxicity test results showed that the photodegradation products present in the tested solutions had no growth-inhibiting effects. The decrease in root elongation caused by A was proportional to the residual concentration of I in the photoreaction mixture, a fact that was proved by using B (which is A diluted 1:4) in which I has no more phytotoxic effects (Figure 1).

The above bioassay demonstrated that the sensitized photodecomposed mixture lost its phytotoxicity, indicating the possibility of using this method for the detoxification of I residues in water.

Registry No. I, 1918-16-7; II, 64788-47-2; III, 88036-33-3; IV, 88036-34-4; V, 88036-35-5.

LITERATURE CITED

Acher, A. J.; Dunkelblum, E. *J. Agric. Food Chem.* **1979**, *27*, 1164.
Acher, A. J.; Saltzman, S. *J. Environ. Qual.* **1980**, *9*, 190.
Acher, A. J.; Saltzman, S.; Brates, N.; Dunkelblum, E. *J. Agric. Food Chem.* **1981**, *29*, 707.
Ashton, F. M.; Crafts, A. S. In "Mode of Action of Herbicides"; Wiley: New York, 1973; pp 310–346.
Benton, F. L.; Dillon, T. E. *J. Am. Chem. Soc.* **1942**, *64*, 1128.
Crosby, D. G.; Ming-Yu, L. In "Degradation of Herbicides"; Kearney, P. C.; Kaufman, D. D., Eds.; Marcel Dekker: New York, 1969; p 345.
Elad, D.; Rao, D. V.; Stenberg, V. I. *J. Org. Chem.* **1965**, *30*, 3252.
Gramlich, W. *Liebigs Ann. Chem.* **1979**, 121.
Harris, G., Ed. "Dictionary of Organic Compounds"; Oxford University Press: New York, 1965; Vol. 4, p 2583.
Jaworski, E. G. In "Degradation of Herbicides"; Kearney, P. C.; Kaufman, D. D., Eds.; Marcel Dekker: New York, 1969; pp 174–177.
Klendgen, H. K. *Weed Res.* **1980**, *20*, 41.
Martin, H., Ed. "Pesticide Manual"; British Crop Protection Council: London, 1972; p 411.
Rejtö, M.; Saltzman, S.; Acher, A. J.; Muszkat, L. *J. Agric. Food Chem.* **1983**, *31*, 138.
Saltzman, S.; Acher, A. J.; Brates, N.; Horowitz; M.; Gevelberg, A. *Pestic. Sci.* **1982**, *13*, 211.
Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
Stolle, R. *J. Prakt. Chem.* **1930**, *128*, 1.
Walker, J.; Daisley, R. W.; Beckett, A. H. *J. Med. Chem.* **1970**, *13*, 983.

Received for review March 14, 1983. Revised manuscript received September 21, 1983. Accepted October 24, 1983. This study was supported, in part, by a grant-in-aid from the United States–Israel Binational Agricultural Research and Development Fund (BARD). Contribution from the Agricultural Research Organization, The Volcani Center, Bet Dagan, Israel. No.668-E, 1983 series.