

# Photochemistry of Pendimethalin

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Pendimethalin decomposed readily when irradiated in methanol at wavelengths  $\lambda \geq 250$  nm to form a number of products. In addition to the N-dealkylated intermediates, the principal products were 2-methyl-4,6-dinitro-5-[(1-ethylpropyl)amino]benzaldehyde and 2-methyl-4,6-dinitro-5-[(1-ethylpropyl)amino]benzyl alcohol. The decomposition at sunlight wavelengths ( $\lambda \geq 290$  nm) in methanol is relatively slower and also leads to N-dealkylation and arylmethyl oxidation. Neither acid nor alkali has an effect on the rate of disappearance of pendimethalin. At acidic pH N-dealkylation takes place, whereas at alkaline pH one of the NO<sub>2</sub> groups is replaced by an OH group.

Pendimethalin [*N*-(1-ethylpropyl)-2,6-dinitro-3,4-xylydine, I (Figure 1)], a representative member of a growing list of N-substituted 2,6-dinitroanilines, is a selective herbicide that controls most annual grasses and certain broad-leaved weeds in cotton, soybean, and other crops. Soil persistence studies (Savage and Jordan, 1980) of this chemical indicated relatively rapid breakdown (half-life 4-6 days), while Walker and Bond (1977) reported a longer persistence in soil (half-life 72-172 days) with the persistence related to the moisture, temperature, and organic matter of the soil. Earlier studies (Parochetti and Dec, 1978) of the photodecomposition of I in soil exposed to sunlight showed much lower conversion (9.9% in 7 days) than other dinitroaniline herbicides previously studied (Leitis and Crosby, 1974). Recently, a number of photoproducts were identified when I was irradiated in methanol for 48 h ( $\lambda = 300-400$  nm). Photodecomposition was reported to involve oxidative dealkylation, nitro reduction, and cyclization (Dureja and Walia, 1989). A chemical present in the environment may undergo direct and indirect photochemical transformations. The latter may include photosensitized degradation, oxygenation, and photoinduced transformation. Earlier studies (Parochetti and Dec, 1978; Dureja and Walia, 1989) on the photodecomposition of I ( $\lambda \geq 300$  nm) in solution and adsorbed on soil probably involve indirect photochemical processes. To our knowledge, very little is known about the photochemistry of I at its maximum UV absorption ( $\lambda \leq 250$  nm). In the present work a comparative study of the photodecomposition of I under artificial sunlight exposure ( $\lambda \geq 290$  and 250 nm) in an organic solvent (MeOH) is reported. In addition to this, the effect of pH on the rate of degradation of I at  $\lambda \geq 290$  nm is also examined.

## EXPERIMENTAL PROCEDURES

**Materials.** Pendimethalin was obtained from Riedel-de-Haen, FRG, and was purified by repeated crystallization from methanol, mp 56 °C (99% HPLC pure). 6-Nitro-3,4-xylydine (97% purity) was provided by Aldrich Chemical Co. and was used for comparison without purification. All the solvents used were of AR grade.

**Apparatus.** The rate of disappearance of the pesticide was measured by a HPLC, Gibson-Abimed Model 302, equipped with a Shandon reverse-phase column (RP-18, 25 × 0.4 cm) and a UV detector set at 240 nm; methanol was used as the mobile phase at a flow rate of 1 mL/min. Photoproducts were separated with

a preparative HPLC, Gibson-Abimed Model 305, equipped with a microsorb C-18 reverse-phase column (Rainin Instruments Co., 25.0 × 1.0 cm) and a UV detector with wavelength set at 240 nm.

Mass spectra were obtained on an LKB spectrometer Model 900 from LKB Produkter, Bromma, Sweden, using direct inlet system and a GC-MS, Hewlett-Packard (HP) Model 59928 at 70 eV. The GC conditions were as follows: an HP capillary column (25 cm × 0.35 mm i.d.) coated with 5% phenyl ethyl silicon, carrier gas helium, temperature program 90-250 °C, 5 °C/min. <sup>1</sup>H NMR (80 MHz) and <sup>13</sup>C NMR (20 MHz) spectra were obtained on Varian CFT-20 spectrometers in deuteriochloroform, and tetramethylsilane was used as an internal standard. IR spectra were taken of KBr pellets by using a Perkin-Elmer Model 577 instrument. All melting points are uncorrected.

**Irradiation Experiments.** I (10 mg, 100 ppm) in 100 mL of methanol was irradiated for 90 min with a high-pressure mercury lamp (HPK 125 W, Philips) jacketed with a water-cooled quartz filter to get maximum intensity of UV light at  $\lambda \geq 250$  nm. Similar experiments with I were carried out in methanol with a Pyrex filter ( $\lambda \geq 290$  nm). The source of light in both experiments was the same. To study the effect of pH on the rate of disappearance, I was dissolved in 20% aqueous methanol irradiated at  $\lambda \geq 290$  nm at pH 5 (adjusted with 0.01 N H<sub>2</sub>SO<sub>4</sub>), 7, and 9 (adjusted with 0.01 M Na<sub>2</sub>CO<sub>3</sub>). The rate of disappearance of I in all of the experiments was directly measured at various intervals of time with an analytical HPLC.

**Isolation and Identification of Photoproducts.** To produce enough of the photoproducts for structure elucidation, 1 g of I in 2 L of methanol was irradiated in four batches (250 mg in 500 mL for 4 h 30 min each time) with a quartz filter. The solutions after irradiation were combined, and the solvent was removed on a rotary evaporator. The concentrated residue, a dark brown oil, was subjected to column chromatography on silica gel (60 mesh, Merck). The column was successively eluted with 2%, 10%, and 25% ethyl acetate in *n*-hexane. Finally, the column was washed with methanol. The fraction eluted with 2% ethyl acetate in *n*-hexane, after concentration on a rotary evaporator, afforded a bright orange solid, which after recrystallization from a mixture of dichloromethane and *n*-hexane yielded bright orange needles (mp 54-56 °C). IR, MS, and NMR spectra were in good agreement with those of pendimethalin (I). The eluates 10% and 25% ethyl acetate in *n*-hexane were found upon HPLC analysis to be mixtures of the same compounds. These fractions were combined, and the solvent was removed at a reduced pressure. The residue was dissolved in 2 mL of methanol and subjected to semipreparative HPLC separation (100  $\mu$ L per injection) using 15% aqueous methanol. Seven main fractions (1-7 in order of increasing retention times) (Table I) were collected. Several milligrams of each fraction were obtained after the corresponding eluates of several injections were combined and the solvent was removed on a rotary evaporator.

**Fraction 1:** yellow solid (*R*<sub>t</sub>, 12.09 min), mp 148-150 °C; mass analysis gave molecular ion at *m/e* 193 (the main mass fragments are recorded in Table I); IR 3300 (NH), 3435 (NH<sub>2</sub>), 1720 (CHO), 935 (NO) cm<sup>-1</sup>; NMR  $\delta$  2.37 (s, 3 H, CH<sub>3</sub> on the aromatic ring),

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**Table I. Preparative HPLC—Retention Time and Mass Spectral Data of Photodecomposition Products of I**

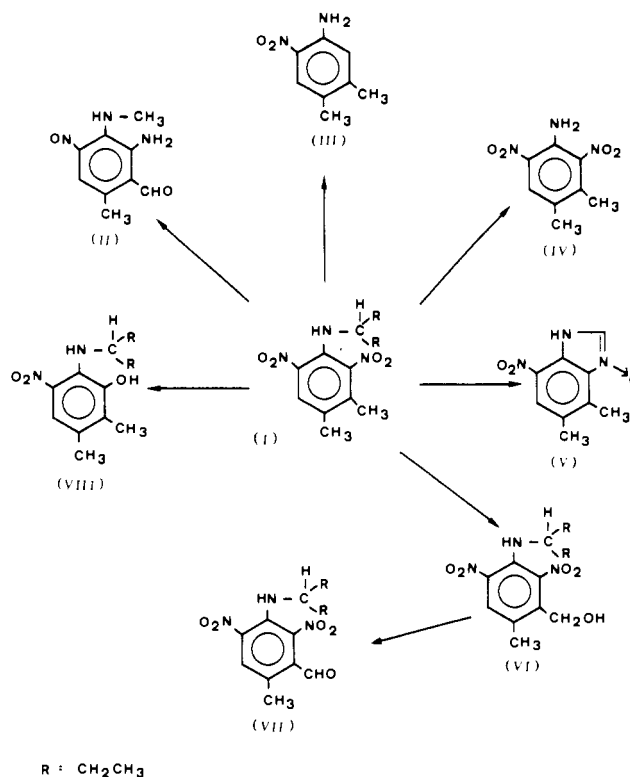
product	retention time, min	mass found	% abundance	structure
II	12.09	193	37.8	M <sup>+</sup>
		178	25.3	M <sup>+</sup> - CH <sub>3</sub>
		165	20.1	M <sup>+</sup> - HCNH
		148	58.6	M <sup>+</sup> - CH <sub>3</sub> - NO
		119	71.0	M <sup>+</sup> - CH <sub>3</sub> - NO - CHO
		77	100.0	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>
III	13.93	166	100.0	M <sup>+</sup>
		150	3.1	M <sup>+</sup> - O
		136	19.8	M <sup>+</sup> - NO
		120	59.4	M <sup>+</sup> - NO <sub>2</sub>
		93	71.3	M <sup>+</sup> - NO <sub>2</sub> - CNH
IV	14.89	211	49.6	M <sup>+</sup>
		194	56.8	M <sup>+</sup> - O - 1
		164	30.9	M <sup>+</sup> - NO <sub>2</sub> - 1
		149	9.4	M <sup>+</sup> - NO <sub>2</sub> - 1 - CH <sub>3</sub>
		134	12.9	M <sup>+</sup> - NO <sub>2</sub> - 1 - 2CH <sub>3</sub>
		118	100.0	M <sup>+</sup> - 2NO <sub>2</sub> - 1
		106	21.6	M <sup>+</sup> - NO <sub>2</sub> - 1 - 2CH <sub>3</sub> - HCNH
V	17.76	207	88.2	M <sup>+</sup>
		191	3.2	M <sup>+</sup> - O
		175	6.3	M <sup>+</sup> - O <sub>2</sub>
		161	14.0	M <sup>+</sup> - NO <sub>2</sub>
		146	61.0	M <sup>+</sup> - NO <sub>2</sub> - CH <sub>3</sub>
		92	12.9	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> + 1
		VI	20.63	297
268	34.2			M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub>
250	12.3			M <sup>+</sup> - NO <sub>2</sub> - 1
224	13.1			M <sup>+</sup> - O - 2C <sub>2</sub> H <sub>5</sub> + 1
206	21.3			M <sup>+</sup> - O <sub>2</sub> - 2C <sub>2</sub> H <sub>5</sub> + 1
77	100.0			C <sub>6</sub> H <sub>5</sub> <sup>+</sup>
VII	23.79	295	3.6	M <sup>+</sup>
		266	24.5	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub>
		250	1.8	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> - O
		222	14.0	M <sup>+</sup> - 2C <sub>2</sub> H <sub>5</sub> - O + 1
		206	9.0	M <sup>+</sup> - 2C <sub>2</sub> H <sub>5</sub> - 2O + 1
		176	11.2	M <sup>+</sup> - 2C <sub>2</sub> H <sub>5</sub> - NO - 2O - 1
		147	7.6	M <sup>+</sup> - 2C <sub>2</sub> H <sub>5</sub> - 2O - NO - CHO + 1
		77	100.0	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>
VIII	41.78	252	21.0	M <sup>+</sup>
		208	7.1	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> - CH <sub>3</sub>
		192	7.7	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> - CH <sub>3</sub> - O
		162	15.4	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> - CH <sub>3</sub> - O - NO
		133	13.0	M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> - CH <sub>3</sub> - NO <sub>2</sub> - C <sub>2</sub> H <sub>5</sub>
77	100.0	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>		

2.36 (s, 3 H, N-CH<sub>3</sub>), 9.55 (s, CHO), 7.39 (s, 1 H, aromatic proton). The spectral data indicated the compound to be 2-methyl-4-nitroso-5-(methylamino)-6-aminobenzaldehyde (II, Figure 1).

**Fraction 2:** yellow crystalline solid (*R<sub>t</sub>*, 13.9 min), mp 139–141 °C; mass at *m/e* 166 (fragments reported in Table I); IR 3380 (NH<sub>2</sub>), 1320, 1520 (NO<sub>2</sub>) cm<sup>-1</sup>; NMR δ 2.17 (s, 3 H), 2.21 (s, 3 H), 7.86 (s, 1 H), 6.38 (s, 1 H), 5.8 (br s, 2 H). MS, IR, and NMR were comparable with the standard 6-nitro-3,4-xylidine (III, Figure 1).

**Fraction 3:** yellow-orange crystals (*R<sub>t</sub>*, 14.89), mp 136–138 °C; mass spectrum *m/e* 211 (parent, fragmentation recorded in Table I); IR 3475, 3360 (NH<sub>2</sub>), 1530, 1340 (NO<sub>2</sub>) cm<sup>-1</sup>; NMR δ 2.17 (s, 3 H), 2.21 (s, 3 H), 8.12 (s, 1 H), 6.68 (br s, 2 H); <sup>13</sup>C chemical shifts at 16.53, 19.34 (arylmethyl carbons), 140.85, 140.06, 131.66, 129.14, 125.54, 136.53 (aromatic carbons) ppm. The data suggest the structure 2,6-dinitro-3,4-xylidine (IV, Figure 1).

**Fraction 4:** yellow-orange liquid (*R<sub>t</sub>*, 17.76 min); molecular peak in MS at *m/e* 207 (parent, fragmentation recorded in Table I); IR 2940 (NH), 1330 (NO<sub>2</sub>), 930 (NO), 1643 (C=N) cm<sup>-1</sup>; NMR δ 2.23 (s, 3 H), 2.16 (s, 3 H), 7.96 (s, 1 H), 6.41 (s, 1 H). These



**Figure 1.** Photoproducts isolated following irradiation of pendimethalin (I) in methanol ( $\lambda > 254$  nm).

spectra can be satisfied only by 7-nitro-4,5-dimethylbenzimidazole 3-oxide (V, Figure 1).

**Fraction 5:** yellow-orange liquid (*R<sub>t</sub>*, 20.63 min); molecular peak at *m/e* 297 (fragments see Table I); IR 3380 (OH), 2970 (NH), 1535, 1330 (NO<sub>2</sub>) cm<sup>-1</sup>; NMR δ 0.88 (t, 6 H), 1.50 (m, 4 H), 3.14 (m, 1 H), 2.41 (s, 3 H), 4.49 (d, 2 H, *J* = 6.5 Hz), 2.04 (s, 1 H), 8.11 (s, 1 H). The NMR spectrum is identical with that of pendimethalin except that the resonance of one arylmethyl group has disappeared and instead the resonance of a -CH<sub>2</sub>OH group is observed. The position of the aromatic proton ( $\delta$  8.1) was the same in pendimethalin and the product, suggesting that the methyl group at position 3 (VI, Figure 1) was oxidized. The structure 2-methyl-4,6-dinitro-5-[(1-ethylpropyl)amino]benzyl alcohol (VI, Figure 1) was further confirmed by <sup>13</sup>C NMR chemical shifts at 66.67 (benzyl alcohol), 18.52 (arylmethyl), 57.73, 28.07, and 9.81 (ethylpropyl) ppm.

**Fraction 6:** red liquid (*R<sub>t</sub>*, 23.79 min); mole peak at *m/e* 295 (fragments recorded in Table I); IR 1710 (C=O), 2975 (NH), 1535, 1335 (NO<sub>2</sub>) cm<sup>-1</sup>; NMR δ 0.88 (t, 6 H), 1.51 (m, 4 H), 3.19 (m, 1 H), 2.44 (s, 3 H), 8.05 (s, 1 H), 10.08 (s, 1 H). The <sup>13</sup>C NMR spectrum showed characteristic chemical shifts for ethylpropyl (58.18, 27.91, 9.73 ppm) and for carbonyl (188.0 ppm). From the NMR spectrum it was observed that the methyl group at position 3 was oxidized to carbonyl, thus suggesting the structure 2-methyl-4,6-dinitro-5-[(1-ethylpropyl)amino]benzaldehyde (VII, Figure 1).

**Fraction 7:** *R<sub>t</sub>*, 41.78 min. The amount of this fraction was so small that, except for mass analysis, no spectral data could be obtained. From the mole peak at *m/e* 252 and the main fragments (Table I) structure VIII (Figure 1) is proposed.

## RESULTS AND DISCUSSION

UV irradiation at  $\lambda \geq 250$  nm of a 100 ppm methanol solution of pendimethalin (I, Figure 1) resulted in rapid decomposition (50% in 1.5 h), whereas the compound decomposed slowly (10% in 1.5 h) when irradiated at  $\lambda \geq 290$  nm as shown in Figure 2. The high decomposition rate at  $\lambda \geq 250$  nm is due to direct photolysis near the absorption maximum (240 nm). It is observed that a concentrated solution of I, 250 mg in 250 mL of methanol (3.6 mM), requires a longer time (4.5 h) for 30–40%

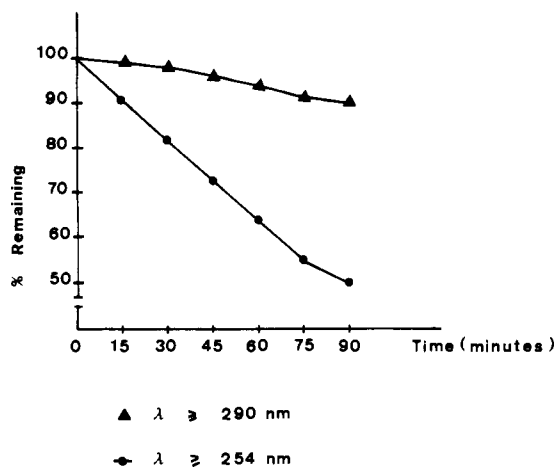


Figure 2. Photodegradation of pendimethalin (100 mg/L) at two different wavelengths.

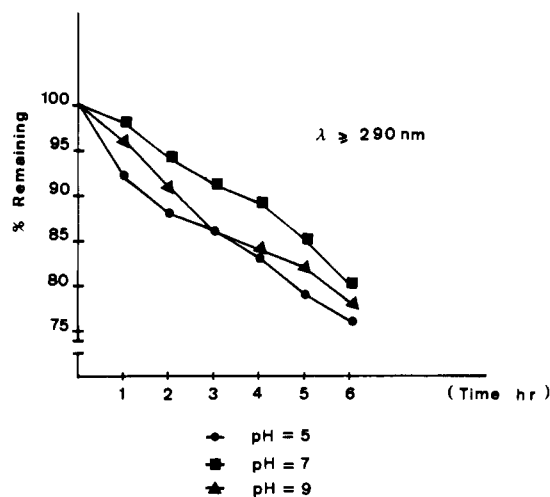


Figure 3. Photodegradation of pendimethalin (100 mg/L) at various pH values.

conversion than a dilute solution (0.36 mM), which requires only 90 min for the same conversion. Here inner filter effects and geometrical factors of the concentrated solution probably lead to slow conversion. As Figure 3 indicates, there was no marked dependence of the conversion of I (100 ppm) on pH. However, different products were obtained. Under acidic and neutral conditions, IV was found to be a major photoproduct, followed by III as a minor one. Compound VIII was identified as the major product at alkaline pH, as is consistent with the observation of Havinga and Kronenberg (1968). A photolyzed methanol solution of I revealed on HPLC analysis more than 25 products. Column chromatographic fractionation of the ethyl acetate/*n*-hexane fraction on silica gel and semi-preparative HPLC separation on an RP-18 reverse-phase column afforded seven compounds (II-VIII, Figure 1). Compound IV, VI, and VII are the major photoproducts, followed by II, III, and V, and product VIII was a minor one. The photodecomposition of pendimethalin involves mainly N-dealkylation and arylmethyl oxidation in addition to processes like nitro group reduction, nitro group elimination, and cyclization. It is suggested that photochemical N-dealkylation of 2,6-dinitroaniline herbicides proceeds via free-radical oxidation by atmospheric oxygen (Leitis and Crosby, 1971; Newsom and Woods, 1973; Plimmer and Klingebiel, 1974). Formation of compounds III and IV (Figure 1) was also observed when the methanol solution of I was photolyzed under a nitrogen atmosphere, suggesting homolytic fission of the nitrogen-carbon bond

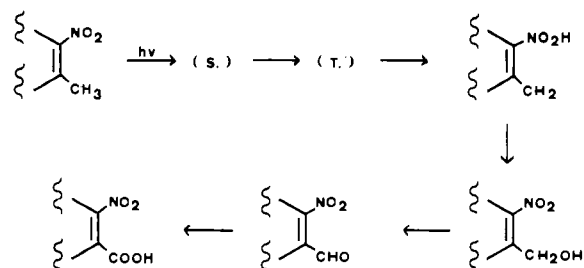


Figure 4. Proposed reaction mechanism of the photooxidation of the arylmethyl group (Katagi, 1989).

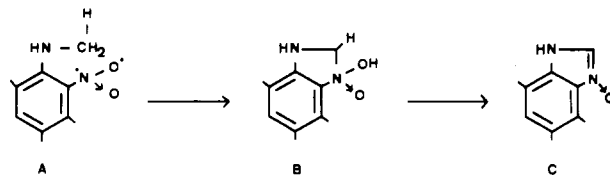


Figure 5. Plausible pathway for the formation of benzimidazole 3-oxide.

and abstraction of a hydrogen radical from the medium, leading to the formation of III and IV. The displacement of the NO<sub>2</sub> group from IV to form III could be explained by either a free-radical (Calvert and Pitts, 1967) or ionic mechanism (Letzinger et al., 1965). The photooxidation of the methyl group at position 3 (VI and VII) could be explained by the mechanism proposed by Katagi (1989) and Greenhalgh and Marshall (1976) for fenitrothion (Figure 4). Photochemical nitro reduction leading to the formation of a nitroso amino derivative (II) probably involves the nitrobenzene radical anion (PhNO<sub>2</sub><sup>-</sup>) or its conjugate acid (PhNO<sub>2</sub>H<sup>+</sup>) as reported by Plimmer and Klingebiel (1974). Leitis and Crosby (1974) proposed a plausible pathway to explain the photochemical formation of benzimidazole N-oxide (V) by slight modification of the free-radical mechanism as proposed by Döpp (1971) (Figure 5). The replacement of the NO<sub>2</sub> group by OH (VIII) could be explained either by a radical process or by photonucleophilic displacement (Havinga and Kronenberg, 1968). Furthermore, product analysis of the methanolic solution of I irradiated at λ ≥ 290 nm for 48 h yielded III, VI, and VII, which were not identified by previous workers (Dureja and Walia, 1989). Previous investigations (Leitis and Crosby, 1974; Newsome and Woods, 1973; Dureja and Walia, 1989) have shown the involvement of photochemical N-dealkylation, nitro reduction, and cyclization of dinitroaniline herbicides. Pendimethalin, a representative of this class of compounds, does undergo the above-mentioned reactions, but its predominant reaction is arylmethyl oxidation.

Considering the photodecomposition of pendimethalin in artificial sunlight to yield polar compounds, it appears reasonable to expect these compounds to be found in soil, plants, or water exposed to the herbicide.

#### ACKNOWLEDGMENT

We are grateful to DAAD (Deutscher Akademischer Austauschdienst) for providing a fellowship to Dr. S. Pal. Our thanks are due to Dr. W. V. Turner for recording <sup>1</sup>H and <sup>13</sup>C NMR spectra and for his helpful discussions.

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Received for review August 2, 1990. Accepted November 19, 1990.