Photodecomposition of Trifluralin

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Trifluralin decomposed readily in water or aqueous methanol at sunlight wavelengths to form a multitude of products. In addition to the minor dealkylated intermediates, the principal product under acidic conditions was 2-amino-6-nitro-α,α,α-trifluoro-*p*-toluidine. At alkaline pH, 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole represented about 80% of the photolysis products within 24 hr. Under all conditions, the highly polar 2,3-dihydroxy-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline and 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-oxide were present in significant amounts but were degraded by heat or further irradiation. The photochemical formation of benzimidazolines, benzimidazoles, and benzimidazole *N*-oxides conforms to a general mechanism which should apply to many dinitroaniline herbicides.

Trifluralin (2,6-dinitro-*N*,*N*-dipropyl-α,α,α-trifluoro-*p*-toluidine, I) is a selective preemergence herbicide representative of a growing list of N-substituted 2,6-dinitroanilines important to weed control. In 1970, 241,000 lb of trifluralin was used in California, while cotton and tomatoes alone employed almost 100,000 lb there in 1972 (California Department of Agriculture, 1970, 1972).

The dinitroanilines are very unstable toward ultraviolet (uv) light. For example, ten products were detected by gas-liquid chromatography (glc) when I was irradiated in anhydrous methanol (Day, 1963), and 2,6-dinitro-*N*-*n*-propyl-α,α,α-trifluoro-*p*-toluidine (VI) and 2,6-dinitro-α,α,α-trifluoro-*p*-toluidine (XII) were tentatively identified by matching retention times. Irradiation of VI in heptane with a high-pressure mercury arc lamp (McMahon, 1966) in turn provided 2-nitro-6-nitroso-α,α,α-trifluoro-*p*-toluidine. Exposure of I in hexane or methanol to laboratory uv light for 24 hr (Harrison and Anderson, 1970) gave products tentatively identified as VI, 2-amino-6-nitro-*N*-propyl-α,α,α-trifluoro-*p*-toluidine, and 2-amino-6-nitro-*N*,*N*-dipropyl-α,α,α-trifluoro-*p*-toluidine. The products from the photodecomposition of I on glass or soil (Wright and Warren, 1965) or in aqueous acetone (Messersmith *et al.*, 1971) remained unidentified.

The outdoor application and subsequent movement of I can result in exposure to sunlight, especially where the herbicide might occur in irrigation water, and preliminary experiments under these conditions indeed revealed rapid photodecomposition to a large array of substances (Leitis and Crosby, 1972). The purpose of the present work was to elucidate the products and pathways of this photodecomposition in sunlight and to positively identify the major products formed by uv irradiation of I in both aqueous and organic media.

EXPERIMENTAL SECTION

Synthesis and Purification of Standards. Technical trifluralin (95%) (Eli Lilly and Co., Indianapolis, Ind.) was recrystallized from absolute ethanol until homogeneous on thin-layer chromatography (tlc) and glc, mp 47–48° (48.5–49°, Probst *et al.*, 1967). 4-Chloro-3,5-dinitro-α,α,α-trifluorotoluene (Eli Lilly) was recrystallized from ethanol, mp 55–57° (56–58°, Hall and Choo-Seng, 1972). Technical *dl*-2-aminobutyric acid (Eastman Organic Chemicals) was recrystallized twice from aqueous ethanol, mp 298–301° (304°, Patai and Zabicky, 1971).

Acetone, benzene, chloroform, ethyl acetate, hexane, methanol, and methylene chloride were redistilled, and ethyl ether was an anhydrous analytical grade (Mallinckrodt). All other chemicals were used in the commercial form.

2-Ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole (III). A solution of sodium sulfide nonahydrate (25 g, 0.1 mol) and sodium bicarbonate (8.4 g, 0.1 mol) in 50 ml of water was added dropwise to a stirred solution of VI (8.8 g, 0.03 mol) in 300 ml of methanol at room temperature during 10 min. The mixture was stirred for 3 hr and poured into 1 l. of water. After 15 min, the suspension was filtered, and the residue washed thoroughly with water, taken up in benzene, and dried. The dried solution was filtered, concentrated to about 200 ml, and held at 5° overnight.

The precipitate was removed by centrifugation, and the supernatant was repeatedly concentrated. The subsequent crops of crystals (3.5 g, 39%) were combined and recrystallized twice from benzene–hexane, mp 79–81°. Further purification by preparative glc (1% SE-30 on Chromosorb W) gave *2-amino-6-nitro-N-propyl-α,α,α-trifluoro-p-toluidine* eluting at 185°, mp 82–83° (82–83°, Emmerson and Anderson, 1966): ir 3472, 3378 (NH$_2$), 1537, 1333 (NO$_2$) cm^{-1}; nmr δ 7.8 (s, Ph), 7.1 (s, Ph), 6.3 (s, NH$_2$), 4.1 (s, NH$_2$), 3.2 (t, CH$_2$), 1.5 (m, CH$_2$), 1.0 (t, CH$_3$).

The diamine (0.3 g, 0.001 mol) was boiled with 10 ml of propionic acid and 20 ml of 4 *N* HCl for 4 hr, cooled, diluted with 120 ml of water, and neutralized with dilute ammonium hydroxide. III was extracted into methylene chloride, dried, concentrated, and purified by preparative glc (2% SE-30 on Chromosorb W) where it eluted at 180–183° as a nearly colorless, viscous liquid which slowly darkened on standing: ir 1536, 1337 (NO$_2$) cm^{-1}; mass spectrum *m/e* 301 (parent and base); nmr δ 8.2 (s, Ph), 8.1 (s, Ph), 4.3 (t, CH$_2$), 3.0 (quadruplet, CH$_2$), 1.7 (m, CH$_2$), 1.5 (t, CH$_3$), and 0.9 (t, CH$_3$); uv $\lambda_{\max}$ 312, 226 nm.

2,6-Dinitro-N-n-propyl-α,α,α-trifluoro-p-toluidine (VI). 4-Chloro-3,5-dinitro-α,α,α-trifluorotoluene (13.5 g, 0.05 mol) in a minimum amount of benzene was added dropwise to a stirred solution of *n*-propylamine (12 g, 0.15 mol) in 100 ml of benzene, stirred at 25° for 4 hr, the benzene washed with water, and the washed solution dried and concentrated until the product precipitated. Recrystallization from benzene provided 12.1 g (83%) of VI, mp 62.5–63° (55–58°, Hall and Choo-Seng, 1972): ir 3356 (NH), 1548, 1326 (NO$_2$) cm^{-1}; nmr δ 8.6 (s, NH), 8.4 (s, Ph), 3.0 (t, CH$_2$), 1.7 (m, CH$_2$), and 1.0 (t, CH$_3$); mass spectrum *m/e* 293 (parent), 264 (base).

2-Ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-Oxide (VII). To 4-chloro-3,5-dinitro-α,α,α-trifluorotoluene (10 g, 0.037 mol) in 110 ml of ethanol was added a solution of α-aminobutyric acid (5.15 g, 0.05 mol) and sodium bicarbonate (5.15 g) in 55 ml of water; the mixture was shaken at 25° for 2 hr, allowed to stand overnight, concentrated to remove most of the ethanol, and diluted to 200 ml with

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water. Unreacted reagent was filtered off and the filtrate extracted with methylene chloride and acidified. The precipitated product was chromatographed on a silicic acid column with chloroform–ethanol (18:1) and the central eluate concentrated to dryness to provide 2.0 g (16%) of *N*-(2′,6′-dinitro-4′-trifluoromethylphenyl)-2-aminobutyric acid as a bright yellow solid, mp 230–231° dec; ir 3356 (NH_2), 1724 (C=O), 1502, 1304 (NO_2) cm^{-1}; nmr δ 8.5 (s, Ph), 2.7 (t, CH), 1.7 (CH_2), 0.8 (t, CH_3); the N-proton was masked by methylene protons.

The intermediate acid (0.1 g) in 1400 ml of 0.5% acetic acid was irradiated at 300–400 nm in a preparative photoreactor (Crosby and Tang, 1969) for 1 hr, acidified to pH 2.0, and extracted with methylene chloride. The extract was subjected to tlc on silica gel G (solvent B), and the band at R_f 0.16 was extracted with acetone; the residue remaining after evaporation of the extracts sublimed at 150–160° (0.01 Torr) to provide VII as the sublimate, mp 215–216° dec: ir 3436 (NH), 2632, 3003–2849 (CH), 1538, 1337 (NO_2) cm^{-1}; nmr δ 8.5 (s, Ph), 8.3 (s, Ph), 3.4 (s, NH or OH), 3.0 (quadruplet, CH_2), and 1.4 (t, CH_3); mass spectrum *m/e* 275 (parent), 259 (base).

2-Ethyl-7-nitro-5-trifluoromethylbenzimidazole (*XI*) was prepared (86% yield) in the same way as III and recrystallized from benzene–hexane, mp 150.5–151°: ir 3344 (NH), 1520, 1335 (NO_2) cm^{-1}; nmr δ 8.4 (s, Ph), 3.1 (quadruplet CH_2), 2.1 (s, NH), 1.5 (t, CH_3); mass *m/e* 259 (parent and base).

2,6-Dinitro-α,α,α-trifluoro-p-toluidine (*XII*). A suspension of 4-chloro-3,5-dinitro-*α,α,α*-trifluorotoluene was stirred with a tenfold excess of concentrated ammonium hydroxide at 50° for 2 hr and then at 70° for 2 hr. The precipitate was filtered off, washed several times with water, and triturated with a small amount of ether to provide a pale yellow solid, mp 142.5–144° (143–144°, Hall and Choo-Seng, 1972): ir 3460, 3356 (NH_2), 1548, 1362 (NO_2) cm^{-1}; mass spectrum *m/e* 251 (parent and base).

2-Amino-6-nitro-α,α,α-trifluoro-p-toluidine (*XIII*). A solution of sodium sulfide (25 g, 0.1 mol) and sodium bicarbonate (8.8 g, 0.1 mol) in 50 ml of water was added dropwise at 25–30° to XII (7.8 g, 0.03 mol) in 500 ml of methanol during 15 min. The mixture was stirred at 25° for 2 hr, filtered, and poured into 1500 ml of water with stirring. The resulting precipitate was filtered off and washed with water; the filtrate was extracted with methylene chloride, and the extract washed with 3 *N* HCl and then water, dried, and evaporated to dryness. The residue and precipitate were combined and recrystallized twice from benzene–hexane, with final purification by preparative tlc on silica gel G (solvent A) to give a red-brown solid, mp 132.5–133.8° (127–128°, Emmerson and Anderson, 1966): ir 3497, 3425, 3378, 3344 (NH_2), 1546, 1335 (NO_2) cm^{-1}; nmr δ 7.8 (s, Ph), 7.2 (s, NH_2), 5.0 (s, NH_2). *Anal.* Calcd for $C_7H_6N_3O_2F_3$: C, 38.0; H, 2.73; N, 19.0. Found: C, 37.7; H, 2.80; N, 18.8.

Chromatography. Tlc was carried out on 20 × 20 cm glass plates coated with 0.5 mm of silica gel G (Stahl) containing 1% of zinc orthosilicate phosphor. The spots and bands were detected by fluorescence quenching under 254-nm light and by visual observation. Bands from preparative tlc were scraped off and extracted three times with warm acetone or ethyl acetate, and the suspensions filtered through a medium porosity fritted glass filter. If tlc was the final purification step, the extracts were dried over anhydrous sodium sulfate, concentrated to 4–6 ml, and centrifuged to remove any silica. The solvent systems used for tlc separations are listed in Table I.

Glc separations were performed on an F and M Model 720 temperature-programmed gas chromatograph equipped with thermal conductivity detector, 60 cm × 0.3 cm i.d. stainless steel columns containing either 1% SE-30 silicone gum on 60–80 mesh, acid-washed, DMCS-treated Chromosorb G or 2% SE-30 on identically treated Chromosorb W, programmed at 7.5°/min from 100 to 280°, injection port and detector temperatures 250 and 300°, respectively, and He flow at 40 ml/min. The eluting compounds were collected from the exit port in glass capillary tubes.

Table I. Solvent Systems for Thin-Layer Chromatography

Acetone–hexane	1:2 (v/v)	Solvent A
Chloroform–ethanol	9:1	Solvent B
Chloroform–ethanol–concd ammonium hydroxide	100:5:0.5	Solvent C
Ether–hexane	3:1	Solvent D
Ethanol–hexane–benzene	1:3:2	Solvent E
Acetone–hexane	1:5	Solvent F
Acetone–hexane–toluene	2:2:1	Solvent G
Benzene–petroleum ether	3:1	Solvent H

Spectra. Spectra were obtained under the following conditions: uv, Beckman DK-2A, methanol solution; nmr (60 MHz), Perkin-Elmer Hitachi R-20, in acetone-*d*, chloroform-*d*, or dimethyl-*d* sulfoxide, TMS internal standard; 100 MHz nmr spectra, Varian HA-100; ir, KBr discs or thin films, Perkin-Elmer 337; mass spectra, Varian M66 (probe); Finnigan 3000 fitted with a 1.2 m × 3 mm i.d. column containing 3% OV-17 on 60–80 mesh Chromosorb W, He flow, 10 ml/min; ionization voltage, 70 eV; high-resolution mass spectra, CEC 110.

Irradiation. A preparative photoreactor (Crosby and Tang, 1969) simulating sunlight conditions provided workable quantities of photolysis products. Solutions initially containing 10–200 mg/l. of I in 10% aqueous methanol were irradiated for periods of a few seconds to 2 days. Air was bubbled in to provide agitation and oxygen, and reactor temperatures were maintained at 30–40°. In some instances, the irradiated solutions were 0.01 *M* in sodium carbonate (pH ~11.0). Irradiations in sunlight were conducted outdoors with 1–50-ppm suspensions of I in deionized or tap water in 4-l. borosilicate glass erlenmeyer flasks, closed with perforated aluminum foil, at Davis, Calif., from June to September 1970. Irradiation times varied from several hours to 1 month, and the temperature of the suspensions occasionally reached a maximum of 48°. Certain of the isolated photolysis products (II, III, VI, VII, and XI) also were suspended in deionized water (10–50 ppm) and exposed to sunlight for 4 days.

Isolation and Identification of Photolysis Products. The sunlight-irradiated solutions of I in water were adjusted to pH 7.0–7.2 with sodium bicarbonate and extracted four times with methylene chloride (neutral extract). The extracted solutions were adjusted to pH 2 with dilute sulfuric acid and again extracted with methylene chloride (acidic extract). The separate extracts were dried (sodium sulfate), concentrated on a rotary evaporator at 30–50°, and fractionated by preparative tlc. The irradiated solutions of identified photolysis products were worked up in the same manner, while solutions from the photoreactor (pH 5.5) were concentrated on the rotary evaporator below 50° before neutralization and extraction.

Neutral Extracts. Preparative tlc (solvent A) resulted in detectable bands, labeled 1–7 in order of decreasing R_f, which were scraped off and eluted with warm acetone and/or ethyl acetate (Table II).

Band 1. The extracted material (R_f 0.69) was purified by glc (1% SE-30): ir 3003–2915 (CH_n), 1550–1323 (NO_2) cm^{-1}; nmr δ 8.0 (s, Ph), 3.0 (t, CH_2), 1.7 (m, CH_2), 0.9 (t, CH_3).

Band 2. The extracted material was purified by tlc (solvent A, R_f 0.63, then solvent F, R_f 0.49), followed by glc (1% SE-30). Ir, nmr, and mass spectra were the same as VI.

Band 3. Rechromatography (solvent G, R_f 0.64, then solvent H) provided a major (R_f 0.36) and a minor (R_f

Table II. Trifluralin Photodecomposition Products

Tlc band	R_f[a]	Elution temp, °C[b]	Mp, °C	Rel amt, %[c]	Identity
1	0.69	160	48		I
2	0.63	156	62	2	VI
3	0.56	240–260	132–136	5	Azoxy compd?
4	0.50	250–261	217	5	Azoxy compd?
		171[d]	142	2	XII
5	0.36		132		XIII
			190–193	25	XIV
6	0.10		Dec	5	Unidentified
7	0.0	173, 183, 192[e]	Liquid	20	II
1A	0.05	160, 168, 171, 185[d,e]	215–216 dec	20	VII

[a] Solvent A. [b] 1% SE-30. [c] 10% aqueous MeOH, 24 hr. [d] 2% SE-30. [e] Decomposition products.

Table III. Thermal Decomposition Products of Compounds II and VII

R_f value[a]					
Solvent A	Solvent D	Elution temp, °C	Mass spectrum, parent m/e	Mp, °C	Identity
		Compound II			
0.54	0.42	183[b]	301	Liquid	III
0.35	0.30	192[b]	317	Liquid	IV
0.63	0.65	173[b]	315	Liquid	V
		Compound VII			
	0.60	160[c]	273	202–204	VIII
	0.20	185[c]	275	138–142	IX
0.49[d]	0.52		257	167–171	X
0.37	0.42	170[c]	259	150–151	XI

[a] Silica gel G. [b] 1% SE-30. [c] 2% SE-30. [d] Solvent E.

0.39) fraction. The investigation of the major fraction will be described elsewhere. The minor fraction was purified by glc (2% SE-30) to give a yellow solid, mp 142°. Ir spectrum was the same as XII.

Band 4. Rechromatography (solvent G, R_f 0.62, then solvent H) provided a major (R_f 0.26) and a minor (R_f 0.07) fraction. The investigation of the major fraction will be described elsewhere; the minor fraction provided a yellow-brown solid in amounts too small to characterize.

Band 5. The extracted material (R_f 0.36) was subjected to tlc (solvent D) providing a major (R_f 0.21) and a minor band (R_f 0.41). The major one was extracted into ethyl acetate, the solution centrifuged and taken to dryness, and the red-brown solid recrystallized from benzene-hexane, mp 132-134°. The ir spectrum was the same as VIII. Reaction with glacial acetic acid and 4 *N* HCl as described for the synthesis of III gave 2-methyl-7-nitro-5-trifluoromethylbenzimidazole whose mp (205.5-207°) and ir spectrum were identical with those of an authentic specimen.

The minor band was extracted into ethyl acetate, concentrated, chromatographed on a silicic acid column, and eluted with benzene-hexane (1:2) to give an orange-red solid (XIV), mp 190-193°: ir 3472, 3356 (NH_2), 3012-2865 (CH_n), 1543, 1337 (NO_2) cm^{-1}; nmr δ 7.4 (s, Ph), 6.4 (s, Ph), 3.0 (s, NH); mass spectrum m/e 261 (parent), 246 (base; P − CH_3). *Anal.* Calcd for $C_{10}H_{10}N_3O_2F_3$: C, 46.0; H, 3.83; N, 16.1. Found: C, 46.2; H, 3.95; N, 16.0.

Band 6. The extracted material (R_f 0.10) was rechromatographed (solvent A, then solvent E, R_f 0.28), extracted into acetone, and taken to dryness to provide a brown amorphous solid. It degraded during tlc or column chromatography to a more polar material, decomposed above 160°, and could not be sublimed or distilled under vacuum: ir 3484 (NH), 3030-2874 (CH_n), and 1389 (NO_2?) cm^{-1}.

Band 7. Extracted material was rechromatographed with solvent A (R_f 0.0) and then twice with solvent C (R_f 0.21). The acetone eluate was concentrated, centrifuged to remove insoluble material, and evaporated under a stream of nitrogen, and the dark red residue (II) was dried *in vacuo* at 25° over phosphorus pentoxide and paraffin shavings and stored in a desiccator in the dark. Alternatively, the entire neutral extract was chromatographed on a silicic acid column and all major products except IX were serially eluted with acetone-hexane at ratios of 1:10, 1:4, and 1:1 (v/v), respectively. The upper third of the column containing IX was extruded, extracted twice with warm acetone and once with warm methanol, and the extracts were purified by preparative tlc twice with solvent C.

II was very difficult to purify because it decomposed on standing, whether neat or in solution. It slowly distilled at 60-70° (0.01 Torr) to give a pale yellow oil which darkened on standing. The pH of a saturated aqueous solution was 0.1 unit above that of control water, and its solubility in water was 25 mg/l. at pH 5.5-7.0, 60 at pH 10.0, and 35 at pH 2.0 with slight darkening. It migrated on silica gel only in the presence of acid or base: ir 3450 (OH), 3003-2900 (CH_n), 1543, 1359 (NO_2) cm^{-1}; nmr δ 8.5 (s, Ph), 8.2 (s, Ph), 4.3 (t, CH_2), 3.3 (quadruplet, CH_2), 1.7 (m, CH_2), 1.5 (t, CH_3), 1.0 (t, CH_3); mass spectrum m/e 317 (maximum), 301 (max − 10), 258, 213 (base). *Anal.* Calcd for $C_{13}H_{16}N_3O_4F_3$: C, 46.6; H, 4.81; N, 12.5. Found: C, 47.9; H, 4.80; N, 12.6.

Thermal and Photochemical Decomposition of II. II decomposed above 70°. Three major volatile products were formed by heating it above 200° in a glass vessel or hot glc column and were separated by tlc (solvent A) and purified by glc (1% SE-30). They were collected as viscous liquids (Table III) with the following spectra.

Compound III. See the section on standards.

Compound IV. Ir 3370 (OH), 3135-2907 (CH), 1546, 1337 (NO_2) cm^{-1}; nmr δ 8.3 (s, Ph), 8.2 (s, Ph), 5.2 (quadruplet, OCH), 4.4 (t, CH_2), 3.0 (m, CH_2), 1.8 (d, CH_3), 1.6 (t, CH_3); mass spectrum m/e 317 (parent), 260 (base); exact mass calcd for $C_{13}H_{14}F_3N_3O_3$, 317.0987; found, 317.0933.

Compound V. Ir 3115-2907 (CH_n), 1709 (CO), and

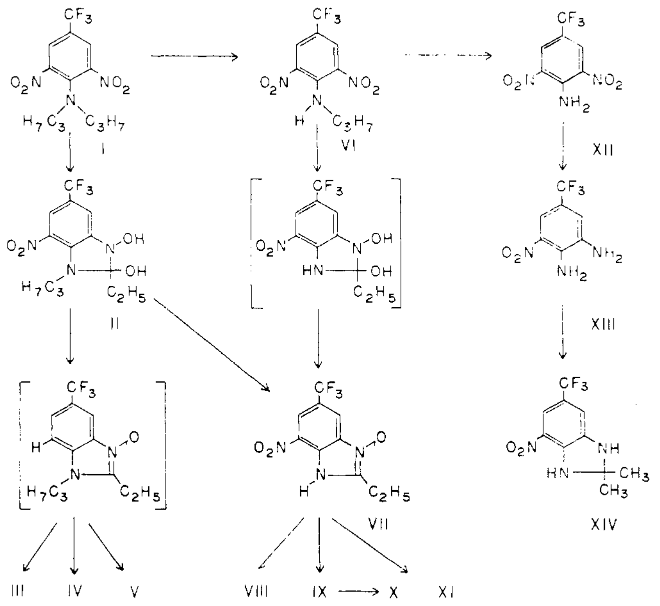


Figure 1. Photodecomposition of trifluralin.

1541, 1339 (NO_2) cm^{-1}; nmr δ 8.1 (s, Ph), 7.9 (s, Ph), 4.5 (t, CH_3), 2.7 (s, isolated CH_3), 1.6 (m, CH_2), 0.9 (t, CH_3); mass spectrum m/e 315 (parent), 257 (base).

An aqueous suspension of II was exposed to sunlight in the same manner as I. The extracted neutral products were subjected to tlc in solvents A and D, and the acidic products in solvents A, B, and E.

Acidic Extracts. After fractionation by tlc with solvent A, the single main band (R_f 0.05) was developed with solvent G (R_f 0.34) and then solvent B (R_f 0.15). The purified material was crystallized from acetone–benzene and dried *in vacuo* at 25° over phosphorus pentoxide and paraffin shavings to provide VII as white crystals, mp 215–216° dec, sublimation 130° (0.01 Torr), which were stable at 25° in a dark desiccator or vial up to several months: ir 3436 (NH), 2632, 3003–2849 (CH_n), 1538, 1337 (NO_2) cm^{-1}; mass spectrum m/e 275 (parent), 274 (P − H), 259 (P − O), 258 (base) (P − OH). *Anal.* Calcd for $C_{10}H_8N_3O_3F_3$: C, 43.6; H, 2.93; N, 15.3. Found: C, 43.2; H, 2.9; N, 14.7. Satisfactory nmr spectra were not obtained.

VII reacted vigorously with diazomethane in ether to give primarily a white solid (XV), mp 115–116°: ir 3086–2890 (CH_n), 1534, 1335 (NO_2) cm^{-1}; mass spectrum m/e 289 (parent), 270 (base); nmr δ 8.4 (s, Ph), 8.0 (s, Ph), 4.3 (s, isolated CH_3), 1.1 (quadruplet, CH_2), 1.5 (t, CH_3). XV partially decomposed to XI on hot glc columns.

Thermal and Photochemical Decomposition of VII. VII formed four volatile products when heated above its melting point in a glass vessel or a hot glc column. They were separated by tlc (solvent D) and rechromatographed with the same solvent, and VIII and XI were further purified by glc (2% SE-30). All were white solids (Table III) with the following spectra.

Compound VIII. Ir 3300 (NH), 3100–2900 (CH_n), 1701 (CO), 1538, 1330 (NO_2) cm^{-1}; nmr δ 8.7 (s, Ph), 8.6 (s, Ph), 3.9 (s, NH), 2.8 (s, isolated CH_3); mass spectrum m/e 273 (parent and base).

Compound IX (minor). Ir 3195 broad (OH), 3100–2882 (CH_n), 1527, 1328 (NO_2) cm^{-1}; nmr δ 8.4 (s, Ph), 5.3 (quadruplet, OCH), 3.1 (s, NH or OH), and 1.7 (d, CH_3); mass spectrum m/e 275 (parent), 186 (base).

Compound X. Ir 3367 (NH), 3096–2890 (CH_n), 1517, 1333 (NO_2) cm^{-1}; nmr δ 8.4 (s, Ph), 8.0 (s, Ph), 7.1 (d of d, CH), 6.7 (d of d, CH_2), 5.9 (d of d, CH_2), 2.9 (s, NH); mass spectrum m/e 257 (parent), 211 (base).

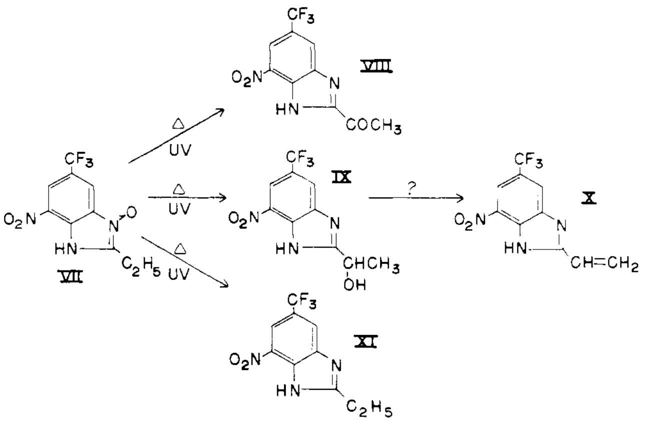


Figure 2. Thermal and photochemical degradation of VII.

Compound XI. See the section on standards.

Irradiation of VII was the same as for II.

RESULTS

Trifluralin was very unstable to sunlight, especially in the presence of an organic solvent. Its homogeneous solutions in 10% aqueous methanol contained the monodealkylated photoproduct VI after only about 30 sec in light, accompanied by a color change from pale yellow to dark yellow-brown during several hours in which tlc revealed the formation of over 20 products. Suspensions of I in water gave the same products but at a slower rate; VI became detectable within about 1 hr.

The dinitrotoluidines VI and XII tentatively identified by Day (1963) were confirmed (Table II), but the others suggested by Harrison and Anderson (1970) specifically were not detected under our conditions. Within a few minutes, the principal photodecomposition products formed in aqueous methanol or water consistently were 2-amino-6-nitro-α,α,α-trifluoro-p-toluidine (XIII) (plus the artifact XIV derived from its reaction with acetone) and two unusual, highly polar compounds characterized as 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-oxide (VII) and 2,3-dihydroxy-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline (II) (Figure 1). Two other products appeared to be azoxybenzenes and will be described at a later date.

Identification of VII. Initial evidence for the structure of VII came from examination of its thermal breakdown products VIII, IX, X, and XI. XI was shown to be 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole by analysis and comparison of its physical properties with those of a synthesized standard (Figure 2).

The carbonyl absorption of VIII at 1701 cm^{-1} suggested a methyl aryl ketone, as did the nmr singlet at δ 2.8. Considering the parent mass, the formation of XI from VII, and the NH absorption at δ 3.9, VIII must be 2-acetyl-7-nitro-5-trifluoromethylbenzimidazole. The olefinic protons in the nmr spectrum of the similar compound X comprised an AMX system where J_{MX} = 18 Hz, J_{AX} = 10 Hz, and J_{MA} = 2 Hz; considering the parent mass, X must be 2-vinyl-7-nitro-5-trifluoromethylbenzimidazole. The quadruplet at δ 5.3 in the nmr spectrum of IX, equivalent to one proton, was considerably shifted from the normal position (δ 3.0) for methylene protons of closely related standards such as XI and suggested the presence of an oxygen atom on the same carbon. These and the other spectral data indicated that IX must be 2-(α-hydroxyethyl)-7-nitro-5-trifluoromethylbenzimidazole.

The thermal degradation products suggested that VII was 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole 3-oxide, and the spectra, molecular weight, and chemical properties all agreed with the *N*-oxide structure. For ex-

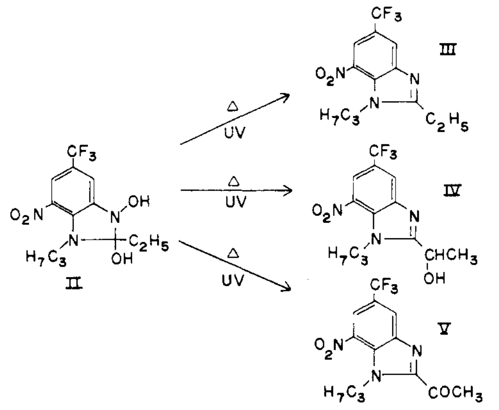
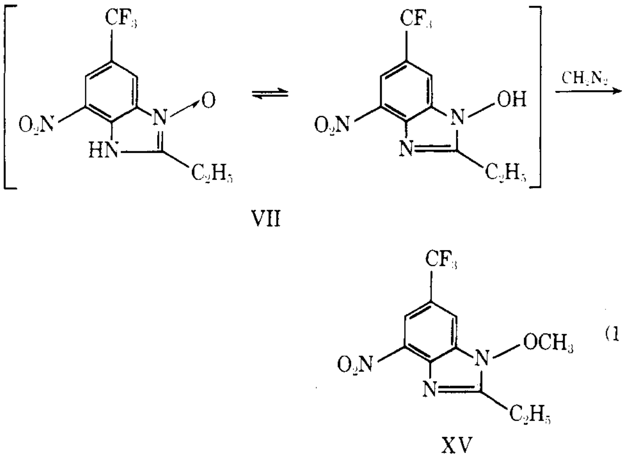


Figure 3. Thermal and photochemical degradation of II.

ample, tautomerism caused 2-carbomethoxy-5-nitrobenzimidazole 3-oxide to give a yellow solution in base and a colorless solution in acid (Luetzow *et al.*, 1966); VII behaved identically, while the other benzimidazoles did not give color and did not dissolve in base. Methylation of benzimidazole 3-oxide was reported to give a mixture of 1-methylbenzimidazole 3-oxide and 3-methoxybenzimidazole (Hayashi *et al.*, 1960), and reaction of VII with diazomethane likewise provided a major product XV whose molecular weight (289) coincided with monomethylation. Breakdown of XV to give XI on a hot glc column suggested that diazomethane had reacted with the hydroxylamine tautomer to give 2-ethyl-1-methoxy-4-nitro-6-trifluoromethylbenzimidazole (eq 1).



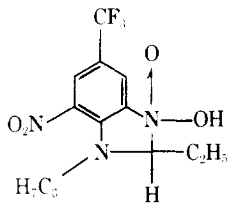
The photodecomposition products of VII were the same as those produced by heat. Loss of oxygen from aromatic amine *N*-oxides is generally observed upon photolysis (Spence *et al.*, 1970); for example, 1-benzyl-2-ethylbenzimidazole 3-oxide was deoxygenated by light (Ogata *et al.*, 1970) to form the corresponding benzimidazole analogous to the observed formation of XI from VII. Light also induces rearrangement of aromatic amine *N*-oxides to alcohols and ketones, and photolysis of 2,3-cyclopentenoquinoline *N*-oxide gave a high yield of 1,2,3,4-tetrahydrocarbazol-4-one (Spence *et al.*, 1970) while pyridine-2-methanol resulted from the uv irradiation of 2-picoline *N*-oxide (Hata and Tanaka, 1962). Accordingly, VII provided the alcohol IX (which dehydrated thermally to the olefin X) as well as the ketone VIII.

The photolysis of *N*-2,4-dinitrophenyl derivatives of amino acids at 360 nm in aqueous media (Neadle and Pollitt, 1969) provides a convenient route to 5-nitrobenzimidazole 3-oxides with a variety of 2 substitutents. The procedure was found to be equally effective for synthesis of benzimidazole oxides from dinitrotrifluoromethylphenyl (DNT) amino acids (Crosby and Bowers, 1968), and VII proved to be identical with the compound prepared by photolysis of *N*-(2′,6′-dinitro-4′-trifluoromethylphenyl)-2-aminobutyric acid (XVI) by the method of Neadle and Pollitt (1967), thus confirming its structure.

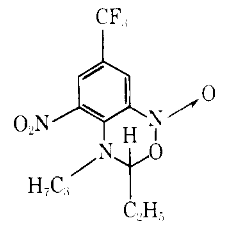
Table IV. Uv Absorption Characteristics of Trifluralin Photolysis Products[a]

Compd	λ_{max}, nm	$\epsilon \times 10^{-4}$	λ_{max}, nm	$\epsilon \times 10^{-4}$
II			247	0.9
III	312	5.0	226	0.5
IV	310	6.0	228	0.9
V	321	16.0	254	0.3
VII	322	5.0	255	0.8
VIII	320	1.4	254	0.3
IX	312	6.4	229	0.7
X	322	4.4	229	0.8
XI	311	6.6	224	0.4

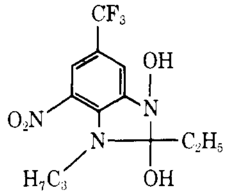
[a] Methanol solution.



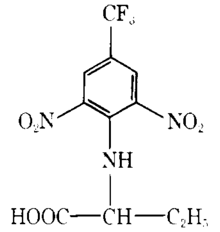
IIa



IIb



IIc



XVI

Identification of II. The structure of II was suggested by that of VII as well as by the thermal breakdown products III, IV, and V (Figure 3). Spectra and comparison with a synthesized standard proved III to be 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole. The spectra and molecular weight of IV excluded all but two structures: 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole 3-oxide and 2-(α-hydroxyethyl)-7-nitro-1-propyl-5-trifluoromethylbenzimidazole. Absence of a strong P − 16 peak in the mass spectrum was inconsistent with the *N*-oxide structure (Tatematsu *et al.*, 1967) and, as with IX, the quadruplet at δ 5.2 equivalent to a single proton (a downfield shift of 2 δ) indicated attachment of oxygen at the methine carbon of the carbinol structure. Spectral data likewise indicated that V was the corresponding methyl ketone.

The similarity of the thermal decomposition products and mass spectrum of II to those of VII suggested that it, too, was a benzimidazole *N*-oxide, but its uv spectrum (Table IV) showed none of the 310-322-nm absorption characteristic of the related benzimidazoles and their oxides. Instead, the data were consistent with a saturated structure which readily underwent elimination of water (as in the mass spectrometer) to generate a benzimidazole *N*-oxide, and combustion analysis conformed to any of three plausible compounds (IIa-IIc). IIa, a form of nitronic acid, should be at least as acidic as a carboxylic acid (Nielsen, 1969); the slightly basic solution and weakly amphoteric properties of II were more consistent with the other structures. The absence of a singlet above δ 3.5 in the nmr spectrum precluded structure IIb; integration indicated the expected 16 protons, with the two hydroxyls masked by CH_2 and CH_3 absorption (Newsom and Woods, 1973), an interpretation which might be verified by deuterium exchange. Cyclic diol absorption (3450 cm^{-1}) in the ir spectrum of neat, anhydrous II supported the chemical and spectral evidence for IIc.

Other Photodecomposition Reactions. Although the major products formed by irradiation of I were the same whether water or methanol was employed as solvent, the relative amount of II decreased and that of VII increased in water. The number and amount of minor, colored, polar products increased in the presence of methanol. Likewise, the ratio of products changed with pH. A colorless, strongly quenching band just above band 3 in the neutral extract of I irradiated at pH 11.0 was collected after rechromatography twice with solvent D and glc (2% SE-30) as a white solid, mp 149-151°, identified by mixture melting point and its ir spectrum as 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole (XI). Within 24 hr, it constituted 70-80% of the total photoproducts, with II, VII, and XIII each accounting for an additional 5%.

To verify the reaction sequence (Figure 1), several of the photolysis products were exposed to sunlight. The major photoproduct from VI, isolated from the acidic extract of an irradiated aqueous suspension by the procedure for the acidic extract from irradiated I, was a white solid identical with VII by tlc with solvents A, B, and E, thermal decomposition pattern on glc, and ir spectra. XIII was present in the neutral extract.

A suspension of II in water was completely degraded by sunlight in 4 days; tlc revealed the thermal degradation products III, IV, and V based on R_f values in solvents A and D. The acidic extract contained the benzimidazole *N*-oxide VII (10% yield), identified by tlc with solvents A, B, and E, and glc degradation pattern (2% SE-30). In turn, III and IV were themselves completely photolyzed by sunlight in 4 days.

A suspension of VII in water remained 30-40% unreacted after sunlight irradiation for 4 days and was recovered from the acidic extract. The neutral extract gave one major product, whose identity remains unknown, and three minor products corresponding to the thermal degradation products VIII, IX, and XI based on R_f values in solvents A and D. Irradiation of XI showed it to be very stable to light; approximately 70% was recovered unchanged after 4 days, although two major and four minor products were observed by tlc in solvent D. VII was relatively stable at pH 11, and no XI was observed as a photolysis product.

DISCUSSION

The photodecomposition of trifluralin involves oxidative dealkylation, nitro reduction, and cyclization. The photochemical N-dealkylation, like that of monuron (Crosby and Tang, 1969), zectran, and matacil (Abdel-Wahab and Casida, 1967), appears to be a free-radical oxidation by atmospheric oxygen (Sharkey and Mochel, 1959); the reduction in methanol represents the well-known abstraction of hydrogen atoms from the medium (Plimmer, 1970; Crosby and Hamadmad, 1971), although the mechanism of photoreductions in water is not clear (Crosby, 1972a).

A modification of the free-radical mechanism proposed by Doepp (1971) to explain the photochemical formation of indole *N*-oxides from nitroaralkanes provides a plausible route from 2-nitroanilines to the benzimidazoles (Figure 4). The apparently facile abstraction of H atoms from the *N*-alkyl group which leads to dealkylation also should encourage the rapid formation of B (and perhaps C) from the light-excited A; McMahon (1966) reported that dinitroanilines such as VI are converted photochemically to aldehydes and 2-nitrosoanilines (E), logically through D, and Russell (1965) showed that the nitrosoanilines undergo aldol condensation with aldehydes under mild conditions to provide the corresponding benzimidazole *N*-oxides (F). The dehydration of F is exactly analogous to the synthesis of nitrones from ketones and N-substituted hydroxylamines (Exner, 1951). Where R = H, F should be easily dehydrated to the resonance-stabilized G, while it should be relatively stable when R = alkyl.

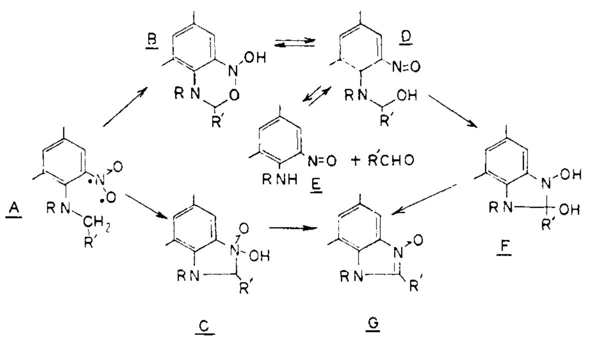


Figure 4. Proposed mechanism of dinitroaniline herbicide photolysis.

The mechanism is quite general for the dinitroaniline herbicides. Those similar to I in their alkylation pattern should form type F compounds and benzimidazoles readily, as indeed does dinitramine (2,6-dinitro-*N,N*-diethyl-3-amino-α,α,α-trifluoro-*p*-toluidine) (Newsom and Woods, 1973); where there is chain branching adjacent to the N, compounds such as C and E should predominate, as shown with dibutalin (*N-sec*-butyl-4-*tert*-butyl-2,6-dinitroaniline) (Plimmer and Klingebiel, 1972). The mechanism may be ionic as well as radical (Meth-Cohn and Suschitzky, 1972), especially after the first step, perhaps explaining the formation of XI in alkaline media.

Considering the opportunities for dealkylation, reduction, and cyclization also available to the reactive intermediates of trifluralin photolysis, the eventual photodecomposition of the herbicide to a largely unresolvable mixture of numerous trace products is understandable. In the laboratory, the relative stability of three of the compounds—VII, XI, and XIII—became apparent, but the known reactivity of 1,2-phenylenediamines with sugars (Heath and Roseman, 1963), acids (Pool *et al.*, 1937), and ketones (as demonstrated by formation of XIV during extraction and chromatography) suggests that XIII might react readily with environmental reagents under field conditions. Although the photoreduction required for its formation predictably is enhanced by an organic medium, the reaction obviously proceeds even in pure water (Nakagawa and Crosby, 1971; Crosby *et al.*, 1972).

The dealkylated benzimidazole XI, most stable of the photoproducts, might persist in the environment long enough to be detectable as was the case with the corresponding compound from dinitramine (Smith, 1972). At alkaline pH, XI became the principal trifluralin photolysis product, and exposure of I vapor to uv light provided XI, together with VI (Moilanen and Crosby, 1972).

As in previous investigations with dinitroaniline herbicides, the present work was severely complicated by the presence of "polar products" such as II and VII. Polar compounds also were reported to represent the terminal decomposition products of I in both aerobic and wet anaerobic soils (Probst *et al.*, 1967), together with VI, XII, XIII, and related amines. Considering the presence of free radicals in soil (Steelink and Tollin, 1967) to initiate the simple reactions of Figure 4 instead of light, it appears reasonable that benzimidazolines and benzimidazole *N*-oxides may occur in trifluralin-treated soil, and the repeated similarity between the products of photodecomposition and of metabolism (Crosby, 1972b) suggests that the same may be true of the "polar products" found in plants and rumen fluid (Probst and Tepe, 1969) exposed to the herbicide.

The consistent thermal decomposition pattern of II and VII on glc could be utilized to detect their presence in the immobile fractions from tlc. Otherwise, however, the present investigation demonstrates clearly that reliance upon glc for identification, as in previous trifluralin investigations, can introduce artifacts and obscure the major photolysis products.

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