The Photodecomposition of Trifluralin in Water

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The widely used herbicide, trifluralin (2,6-dinitro-N,N-dipropyl-α,α,α-trifluoro-p-toluidine, I) is recognized to be unstable to light (PIECZARKA et al., 1962; DAY, 1963; WRIGHT and WARREN, 1965; HARRISON et al., 1970; MESSERSMITH et al., 1971). However, few photodecomposition products have been even tentatively identified (DAY, 1963; HARRISON et al., 1970) and these only by their gas chromatographic retention times at temperatures approximating 200°C.

The present paper describes an investigation of the photodecomposition of aqueous trifluralin suspensions and solutions by sunlight and identification of major photolysis products isolated by non-destructive techniques.

EXPERIMENTAL

Irradiation. Trifluralin or its photoproducts were suspended in deionized or tap water (50 mg/l) and irradiated in loosely closed Erlenmeyer flasks under summer sunlight in Davis, California, for about 4 days. To obtain larger amounts of photolysis products, a trifluralin stock solution in methanol was diluted to 10 volumes with water to provide 200 mg/l of herbicide and irradiated in a sunlight-simulating photoreactor (CROSBY and TANG, 1969). The pH of the solutions was 5.5; alternatively, pH was adjusted to 7.4 (0.0005 M sodium bicarbonate), 8.2 (0.01 M sodium bicarbonate), or 11.0 (0.1 M sodium carbonate). Optimum yields were obtained in 24-48 hrs.

Columbia sandy loam or Sacramento clay (5 g) was saturated with a 0.1% solution of trifluralin in hexane, the solvent removed by evaporation, and the soil suspended in 100 ml of tap water in the photoreactor (pH 6.5) and irradiated for 4 days.

Isolation and Identification. Irradiated solutions were adjusted to pH 7.0-7.2 with sodium bicarbonate and extracted 4 times with methylene chloride to give the "neutral fraction". The aqueous portion was acidified to pH 2 and again extracted with methylene chloride ("acidic fraction"). Extracts were dried, concentrated under vacuum, and chromatographed.

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The neutral fraction was chromatographed on a column of silicic acid, and nonpolar compounds were eluted with acetone-hexane (1:1 v/v). The upper third of the column was extruded, extracted twice with warm acetone, and the extract was purified by thin-layer chromatography (tlc) twice (silica gel G, $CHCl_3$-MeOH-NH_4OH 200:10:1 v/v), R_f 0.21. Alternatively, tlc (acetone-hexane 1:1 v/v) resolved the 7 major constituents of the neutral fraction; the polar compound remained at the origin. This product was unstable and difficult to purify, although it slowly distilled (60-70°C/0.01 Torr) to give a pale yellow oil (Compound II).

The acidic fraction contained only one major product, purified directly by tlc (silica gel G; acetone-hexane 1:2 v/v, R_f 0.05, followed by acetone-hexane-toluene 2:2:1 v/v, R_f 0.34, and chloroform-ethanol 9:1 v/v, R_f 0.15). The eluted material was crystallized from acetone-benzene, m.p. 215-16°C (Compound V).

Irradiated soil suspensions were filtered; the filtrate was extracted as in the water experiments, while the soil was extracted first with methylene chloride and then with acetone. The separate extracts were dried, concentrated, and examined by tlc as before. Recovery of trifluralin from unirradiated soil was measured by gas chromatography of the combined methylene chloride-acetone extracts (1% SE-30 on 60/80 Chromosorb G).

RESULTS AND DISCUSSION

The photodecomposition of trifluralin was very rapid in aqueous methanol; 6 products were detectable after less than two minutes of irradiation, and about 25 were observed after 3 hours. Photodecomposition in aqueous suspensions, with or without soil, was about one tenth as rapid, but the products were the same. Two of the tentative products from previous

TABLE I.

Effect of pH on trifluralin photodecomposition.[a]

	Proportion (%) at pH			
Photoproduct	5.5	7.4	8.2	11.0
II	20	20	15	5
IV	trace	trace	trace	trace
V	20	20	15	5
VI	0	trace	30	80
VIII	25	25	--	8
Azoxybenzenes	15	15	5	0
All Others	20	20	10	trace
Relative Rate:	90	85	40	10

[a] 10% aqueous methanol, 24 hrs. F40BL lamp.

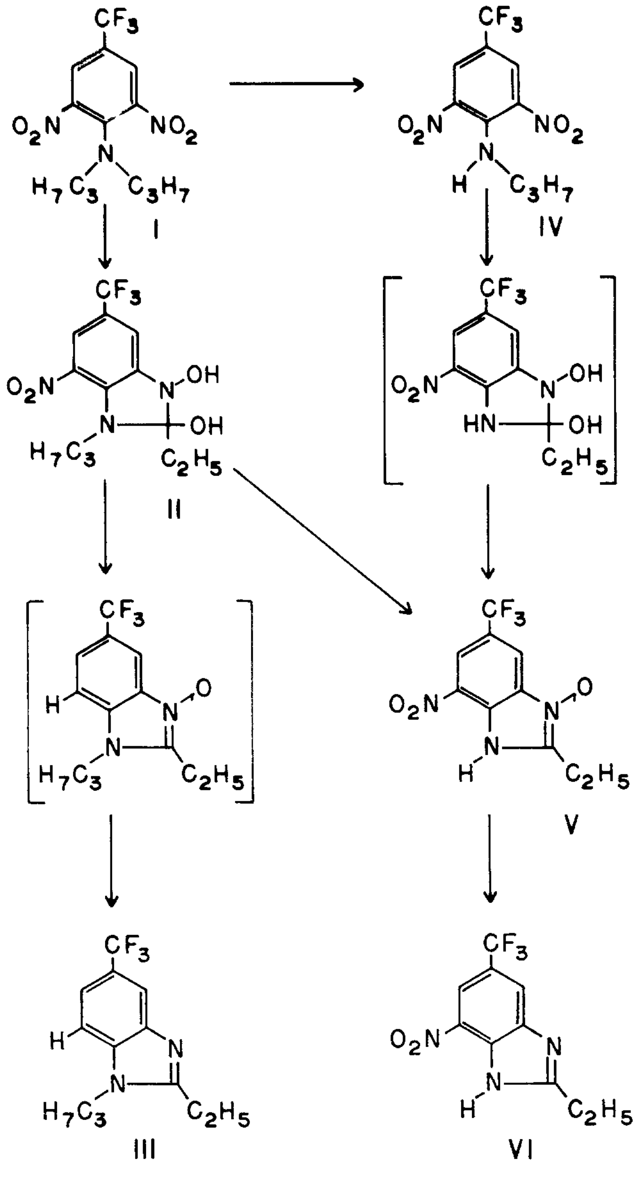

Fig. 1. Trifluralin photolysis.

investigations were confirmed -- 2,6-dinitro-N-propyl-α,α,α-trifluoro-p-toluidine (IV), and 2,6-dinitro-α,α,α-trifluoro-p-toluidine (VII) -- but they appeared only in small amounts (Table I). 2-Amino-6-nitro-α,α,α-trifluoro-p-toluidine (VIII) was the principal product under acidic conditions while 2-ethyl-5-nitro-7-trifluoromethylbenzimidazole (VI) was the principal product in base. Several compounds suspected to be azoxybenzenes also were detected.

Among the consistent major products were two hitherto undetected, highly polar compounds, II and V (Fig. 1). Compound V corresponded to $C_{10}H_8F_3N_3O_3$ by combustion analysis and mass spectrum. The ir and nmr spectra indicated the expected aromatic ring and nitro group, a free NH, and an ethyl group. It absorbed strongly at 322 nm ($\varepsilon = 5 \times 10^4$), and the mass spectrum showed the major peaks at P-1 and P-17 expected of a benzimidazole N-oxide having a free NH. Heating or further irradiation converted V in part to 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole (VI) identical with a synthesized standard, identifying it as the corresponding benzimidazole-3-oxide.

Compound II corresponded to $C_{13}H_{16}F_3N_3O_4$ by combustion analysis, and the ir and nmr spectra revealed the presence of the expected aromatic ring with a nitro group, an n-propyl group, and an ethyl group. However, it did not absorb uv in the 310-320 nm range characteristic of the related benzimidazoles anand N-oxides nor in the 380-400 nm range of trifluralin. The ir spectrum indicated aliphatic-OH absorption characteristic of 1,2-diols, while the mass spectrum was that of the N-propyl benzimidazole N-oxide which would be formed by facile dehydration of II in the mass spectrometer probe. Heating or further irradiation of II gave 2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole (III) identical with a synthesized standard, indicating that II was 2,3-dihydroxy-2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazoline.

Under acidic conditions, photodecomposition to primarily polar products was rapid (Table I), but above pH 7.4 the rate declined sharply and the product proportions changed; the benzimidazole VI became the dominant product at high pH. Although the acidity of natural soils and waters can vary widely between pH 5 and 10 (LYON and BUCKMAN, 1937; STUMM and MORGAN, 1970), the normal values for temperate-zone locations where trifluralin would be applied tend toward pH 6-8. The polar photolysis products therefore could be expected to predominate.

Major products from the irradiation of excess trifluralin on soil suspensions were identical to those formed in water alone at the same pH, and short-term recoveries of trifluralin from the unirradiated soils were essentially quantitative. This suggests that photodecomposition actually occurs in homogeneous solution, despite the low solubility of trifluralin (<1 mg/l according to HULL, 1967), and that the rate will depend upon the adsorption equilibrium between soil and water. This is supported by the extreme rapidity of trifluralin photolysis in aqueous methanol solutions in which, from the identity of the products, the methanol obviously served only as solvent.

The extensive examination of trifluralin degradation in aerobic soil (PROBST et al., 1967) revealed some of the same products (IV, VII, and VIII) we have found in photodecomposition, together with unidentified "polar products". Although it is possible that light could have contributed to their formation, their probable derivation from microbial action may indicate again the similarity of photolysis products to those of oxidative metabolism (CROSBY, 1972) and suggests that II, V, and the related benzimidazoles could occur in soil and water even in the absence of light.

Recently, NEWSOME and WOODS (1973) reported the photochemical conversion of the dinitroaniline herbicide dinitramine to the dihydroxybenzimidazoline and benzimidazole analogous to II, together with other related compounds. It appears, then, that the formation of these polar substances may be of general importance in the environmental transformations of many of the similar dinitroanilines now entering commerce.

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