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Photolysis of the Herbicide Dinitramine (N^3,N^3-Diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine)

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The photolysis of the herbicide dinitramine (N^3,N^3-diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine) in methanol and in water was investigated. The compound was found to degrade rapidly through reductive cyclization of a nitro group and an adjacent N-ethyl group to give the following products: 6-amino-1-ethyl-2-methyl-7-nitro-5-trifluoromethylbenzimidazole; 5-amino-1,2-dihydroxy-3-ethyl-2-methyl-4-nitro-6-trifluoromethylbenzimidazoline; 1-ethyl-6-hydroxylamino-2-methyl-7-nitro-5-trifluoromethylbenzimidazole; and 6-amino-2-methyl-7-nitro-5-trifluoromethylbenzimidazole.

N^3,N^3-Diethyl-2,4-dinitro-6-trifluoromethyl-m-phenylenediamine, dinitramine (1), is a new preplant incorporated selective herbicide which is effective on broadleaf weeds and grasses in cotton, soybeans, and other crops. The products of photolysis of this compound and an idea of the rate of this type of degradation are of interest from environmental and agronomic aspects.

The effect of ultraviolet irradiation on phytotoxic amines with ortho–nitro substituents has been previously studied (Crosby and Li, 1969; Probst and Tepe, 1969). Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine) underwent loss in herbicidal activity and a change in its ultraviolet absorption on exposure to sunlight, both on soil and on glass plates (Wright and Warren, 1965). Unpublished data (Day, 1969) indicate that

photolysis of trifluralin in methanol gave at least ten products. Two of these apparently were the monodealkylated and didealkylated compounds α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine and α,α,α-trifluoro-2,6-dinitro-p-toluidine. A preliminary report of a more extensive reexamination of trifluralin photolysis was presented while this manuscript was in preparation (Leitis and Crosby, 1972).

The present paper describes the degradation rate and products obtained on photolysis of dinitramine (1).

EXPERIMENTAL SECTION

The dinitramine used was recrystallized several times from cyclohexane and ethanol to give >99.6% purity. Solvents were AR grade and melting points were uncorrected.

Rate of Sunlight Degradation of Aqueous Dinitramine. An acetone solution of dinitramine (0.00142 g/cm³) was stirred into 12 l. of water and three 5-ml samples were withdrawn and analyzed (Newsom and Mitchell, 1972) for

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dinitramine, giving 1.06, 1.01, and 1.12 ppm (average, 1.06 ppm). The solution was then poured into a 63 × 81-cm plastic-lined pan (depth, 2.35 cm) in the direct sun at 1:35 p.m. in Southern California. Periodic aliquots were analyzed as follows: 15 min, 0.38 ppm; 30 min, 0.125 ppm; 45 min, 0.028 ppm; 60 min, 0.017 ppm. Aqueous solutions of 1, adjusted to pH values of 5, 7, and 9, were stored in the dark up to 5 months without decomposition

Sunlight Irradiation in Natural Waters. Water samples were collected from the Santa Ana River and the Pacific Ocean in July, 1971. Dinitramine (500 μl of a 10-ppm benzene solution, 5 μg) was added to an 800-ml portion of each water sample in 8 × 14-cm jars. A similar sample was prepared with laboratory deionized water, and the three solutions were exposed to outside sunlight. The samples then were extracted twice with 100 ml of methylene chloride, the extracts were filtered through anhydrous sodium sulfate and evaporated on a Rinco evaporator, and the residue was taken up in 2 ml of benzene. Gas chromatographic analysis gave the following results: amount remaining after 1 hr—ocean, 0.7 μg, river, 0.3 μg, laboratory, 0.2 μg; amount after 2.5 hr—ocean, 0.02 μg, river and laboratory, none detectable; amount after 24 hr—all samples, none detectable.

Sunlight Irradiation on Sand. Twenty-mesh sand was autoclaved, washed several times with methanol, and then dried using a Rinco evaporator. Separate 25-g portions were swirled with 10 ml of a 0.25-ppm dinitramine solution in acetone and the solvent was evaporated. An unexposed sample was analyzed by the standard procedure and showed 1.0 ppm. Samples were then spread on filter papers, approximately a single grain deep, and exposed to direct sunlight starting at 10:30 a.m. on a June day in Southern California. After 4 hr of exposure, 0.16 ppm was found and, after 24 hr, duplicate analyses gave 0.009 and 0.013 ppm of unchanged dinitramine. The low vapor pressure and high soil adsorption of 1 precludes significant loss by volatilization under these conditions.

Photolysis of Dinitramine in Methanol. A 20-g sample of dinitramine was dissolved in 1500 ml of methanol and irradiated for 24 hr with a GE F40/BL bulb (emitting at 300–450 mμ) in a cylindrical pyrex flask surrounding the fluorescent tube. The solution was then transferred to a round-bottomed flask and the solvent removed on a Rinco evaporator. The residual dark oil was taken up in toluene and chromatographed on a silica column, eluting successively with toluene, toluene–chloroform, chloroform, and finally stripping with methanol. Fraction 3 (of 17) contained 12.7 g of unreacted starting material. Fraction 11 was purified by two preparative thin-layer chromatograms on silica with ethyl acetate elution to give 0.11 g of orange solid, mp 101.5–105.5°, which was identified as 6-amino-1-ethyl-2-methyl-7-nitro-5-trifluoromethylbenzimidazole (2). Recrystallization from hexane gave an analytical sample, mp 105–107°.

Anal. Calcd for $C_{11}H_{11}F_3N_4O_2$: C, 45.83; H, 3.82; N, 19.44; mol wt 288. Found: C, 45.89; H, 3.74; N, 19.42.

Mass spectral analysis showed a parent peak at m/e 288 (100%), as well as the fragmentation pattern shown in Table I. The nmr spectrum (Varian Aerograph Model T-60) showed one aromatic proton at δ 8.05 (s), a broad NH_2 at δ 6.05 (s), two methylene protons of the ethyl group at δ 4.2 (q), and three ethyl protons at δ 1.33 (t), with the ring methyl group appearing as three protons at δ 2.65 (s).

The final fraction (No. 17) from the chromatographic column was applied to a silica tlc plate and eluted with methanol. A brown substance at R_f 0.81 was separated from the major fraction at R_f 0.54. The latter was extracted from the scraped plate and the resulting red oil, 0.3 g, was further separated into fraction A at R_f 0 and fraction B at R_f 0.1 after four elutions with acetone. Fraction A

Table I. Mass Spectral Data[a]

Compound 2		Compound 3		Compound 4		Compound 5		Compound 6	
m/e	%	m/e	%	m/e	%	m/e	%	m/e	%
288	100	304	21	260	100	304	7	258	100
242	17	303	11	236	10	289	16	212	47
214	12	288	25	214	63	288	100	208	11
194	14	261	16	194	18	287	13	180	23
42	12	260	59	153	15	245	34	52	12
28	11	247	29	146	11	229	13	28	13
		229	10	126	15	222	13		
		214	22	76	11	217	18		
		194	15	69	12	214	25		
		153	11	52	15	194	18		
		43	100	42	19	173	13		
		42	19	28	13	153	11		
		29	18	18	33	43	86		
		28	10			42	14		
		27	12			19	13		

[a] Only fragments over 10% of base peak are reported.

was assigned structure 3 (5-amino-1,2-dihydroxy-3-ethyl-2-methyl-4-nitro-6-trifluoromethylbenzimidazoline).

Anal. Calcd for $C_{11}H_{13}F_3N_4O_4$: C, 40.95; H, 4.03; N, 17.38; mol wt 322. Found: C, 41.21; H, 3.73; N, 17.36.

The mass spectrum did not show a parent peak at m/e 322, but did exhibit peaks at 304 and 288, corresponding to successive losses of water and oxygen from the relatively unstable molecule. Further mass spectral peaks are listed in Table I. The nmr spectrum showed one aromatic proton at δ 8.4 (s), the two amino protons at δ 6.45 (s), and the ethyl group at δ 4.23 (q) and 1.34 (t). The methyl group was at δ 2.75, and one hydroxyl proton was under each of the $-CH_3$ groups.

Fraction B, above, was assigned structure 5 (1-ethyl-6-hydroxylamino-2-methyl-7-nitro-5-trifluoromethylbenzimidazole).

Anal. Calcd for $C_{11}H_{11}F_3N_4O_3$: C, 43.40; H, 3.62; N, 18.40; mol wt 304. Found: C, 43.50; H, 3.56; N, 17.72.

Mass spectral analysis showed the parent peak at m/e 304. The complete spectrum is listed in Table I. The nmr spectrum showed an aromatic proton at δ 8.28 (s), an ethyl group at δ 4.4 (q) and 1.38 (t), and a methyl at δ 2.70 (s). The protons of the hydroxylamine group were not discernible. Infrared absorptions at 3450, 3120, and 1200 cm^{-1} were indicative of an OH group.

In another photolysis reaction under similar conditions, column chromatographic fraction 4 was evaporated and the residue triturated with aqueous ethanol, leaving unidentified colorless crystals of 6.

Anal. Calcd for $C_9H_5F_3N_4O_2$: C, 41.85; H, 1.94; N, 21.70; mol wt 258. Found: C, 42.18; H, 1.94; N, 21.56.

The mass spectrum showed the parent peak as the base peak at m/e 258. The fragmentation pattern is listed in Table I.

Photolysis of Dinitramine in Water. A 0.1-g sample of dinitramine in 10 ml of acetone was added to 10 l. of water and the resulting suspension (10 ppm) was stirred and irradiated with sunlight in a 5-gal bucket for 2 days. Three 600-ml portions of methylene chloride were then stirred vigorously with the water and the combined organic phases dried over Drierite. The extract was filtered and evaporated, and the residue was taken up in acetone and streaked on a 2-mm silica tlc plate. The plate was eluted successively with 5:1 ethyl acetate-methanol and with toluene. Scraping the color zones and extracting the silica with methanol gave the following fractions, in order of increasing R_f values: (a) 7.5 mg (including 6.1 mg which was obtained from a methanol rinse of the Drierite) of or-
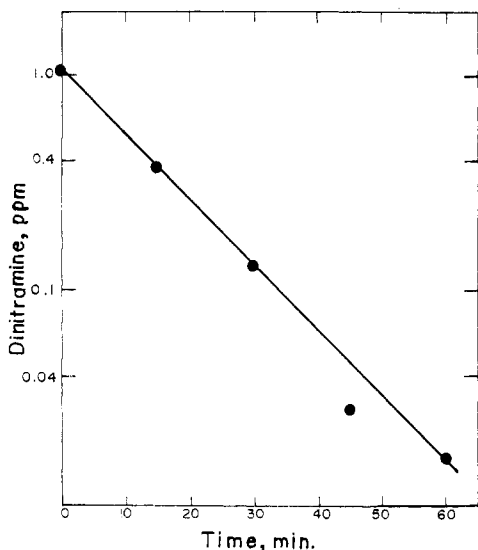
Figure 1. Photolysis of aqueous dinitramine by sunlight.

ange solid with an infrared spectrum superimposable on material previously identified as 5-amino-1,2-dihydroxy-3-ethyl-2-methyl-4-nitro-6-trifluoromethylbenzimidazo-line (3); (b) 1.1 mg of unidentified material which had an infrared spectrum similar to compounds identified from photolysis of methanol solutions of dinitramine; (c) 2.5 mg of solid, identified by infrared and gc retention time as the 6-amino-1-ethyl-2-methyl-7-nitro-5-trifluoromethylbenzimidazole (2) obtained from methanol solutions; (d) trace of sn.eared materials; (e) 4.9 mg of unidentified solid; (f) unreacted dinitramine; and (g) a slight trace of unidentified material.

In another experiment, compound (e) was collected and its mass spectrum obtained (Table I). A parent peak at 260, with losses of 46 (NO_2) and 20 (HF) to the major fragments of 214 and 194 (just as was found with compounds 2 and 3), suggested the compound to be 6-amino-2-methyl-7-nitro-5-trifluoromethylbenzimidazole (4).

Photolysis of Carbon-14-Labeled Dinitramine in Water. An acetone solution of dinitramine labeled with carbon-14 in the trifluoromethyl group (18.6 μCi/mg) was added to 500 ml of water in a petri dish (1.7 cm deep, ca. 0.7 ppm) and two 1-ml samples were withdrawn for scintillation counting in a dioxane–POP cocktail. Values of 0.357 and 0.375 mg of dinitramine/500 ml of solution were obtained. The aqueous solution was placed in the summer sun from 11:00 a.m. to 1:00 p.m., and two more aliquots were counted, indicating 0.354 and 0.339 mg. Two 25-ml aliquots were then removed and extracted with methylene chloride, as in the standard analytical method for dinitramine. Results at this point indicated 0.196 and 0.198 mg (55%) of th· activity in the two organic phases and 0.168 and 0.156 mg (45%) in the two aqueous phases. None of the organic activity appeared as unreacted dinitramine when analyzed on the gas chromatograph.

Photolysis of 5-Amino-1,2-dihydroxy-3-ethyl-2-methyl-4-nitro-6 trifluoromethylbenzimidazoline (3). A sample (0.0395 g) of compound 3, isolated from photolysis of 1, was dissolved in 800 ml of methanol and photolyzed 40 hr with a GE F40/BL bulb. Solvent was then removed and the residue stripped on a tlc plate, along with a reference spot of benzimidazole 2. Elution with 5:1 ethyl acetate–methanol gave five fractions, one of which (R_f 0.87) matched the reference spot. This band was recovered and a portion used for two-dimensional tlc with benzimidazole 2 reference. Mobility of the spots was identical with 5:1 ethyl acetate–methanol and also with 1:4 ethyl acetate–chloroform. Residence time of the major peak on a gas

chromatograph (3% OV-1 at 215°) matched that of authentic benzimidazole 2. The infrared spectra of the two materials were essentially identical.

RESULTS AND DISCUSSION

Sunlight irradiation of a dilute (1 ppm) aqueous solution of dinitramine resulted in rapid decomposition. Exposure to midday May sunlight caused degradation, as indicated in Figure 1, with a half-life of approximately 10 min. This decomposition was a photolytic process rather than simple hydrolysis, since no decomposition was observed for aqueous solutions of dinitramine at pH values of 5, 7, and 9 when stored in the dark for several months.

Sunlight photolysis of dinitramine was found to be rapid also in naturally occurring waters from the Santa Ana River and Pacific Ocean, as was observed in laboratory deionized water. Photolytic degradation also proceeded when solid dinitramine adsorbed on sand was exposed to the sun, although not as rapidly as occurred in solution.

As a prelude to characterization of products from sunlight irradiation, methanol solutions of dinitramine were irradiated (300–450 mμ) in the laboratory, and the products therefrom were isolated and identified. These products were subsequently compared (tlc, ir) with those produced by the action of sunlight on dilute aqueous solutions of dinitramine.

After irradiation, the product mixtures were separated into pure components by column chromatography, thin-layer chromatography, and recrystallization. Irradiation of methanol solutions of 1 produced compounds 2, 3, 5, and 6, shown in Figure 2.

The mass spectrum of compound 2 showed a parent peak at m/e 288. Significant fragments were found at 242 (-NO_2), 214 (-C_2H_4), and 194 (-HF). The molecular weight of 288, together with elemental analysis for C, H, and N, established an empirical formula of $C_{11}H_{11}F_3N_4O_2$ for compound 2. The nmr spectrum indicated one aromatic proton, an ethyl group, and singlets of two and three protons each (-NH_2 and -CH_3). These data can only be satisfied by a benzimidazole structure such as 2 or an isomer thereof. The same compound was also obtained as the principal metabolite in soil decomposition studies, and its structure was confirmed unequivocally by independent synthesis (Smith, 1972). The appearance of a ring-closed product from photolysis of nitro-substituted diamine or aniline herbicides has not been observed heretofore. Under somewhat different conditions, however, the acid-catalyzed photolysis of o-nitrophenyl derivatives of cyclic amines has been reported to form benzimidazoles (Fielden et al., 1970).

Compound 3 was tentatively identified as the dihydroxy analog of 2. Compound 2 is the only cyclized product whose structure is unequivocal. Products 3, 4, and 5 were assumed to be condensed through the 4-nitro group as was established for 2. The mass spectrum of 3 did not have a parent ion at m/e 322, but did show a peak at 304 (-H_2O). Other major fragments were found at 288 (-O), 260 (-C_2H_4), and 214 (-NO_2). Elemental analysis was correct and the nmr was consistent with the proposed structure. The nmr pattern showed one hydroxyl proton broad and partially under the methyl absorption and the other completely under the ethyl triplet. Although a 1,2-dihydroxy benzimidazoline has not been previously reported, the ring structure is apparently stable with electronegative substituents since 1,3-bis(carbobenzyloxy)-2-hydroxybenzimidazoline was prepared from the 1-substituted benzimidazole (Ben-Ishai et al., 1968). The infrared spectrum of 3 exhibited a broad band at 3200 cm^{-1}, consistent with the proposed hydroxylated structure.

Compound 5 showed an unsplit methyl group, as well as an ethyl and an aromatic proton in its nmr spectrum. The
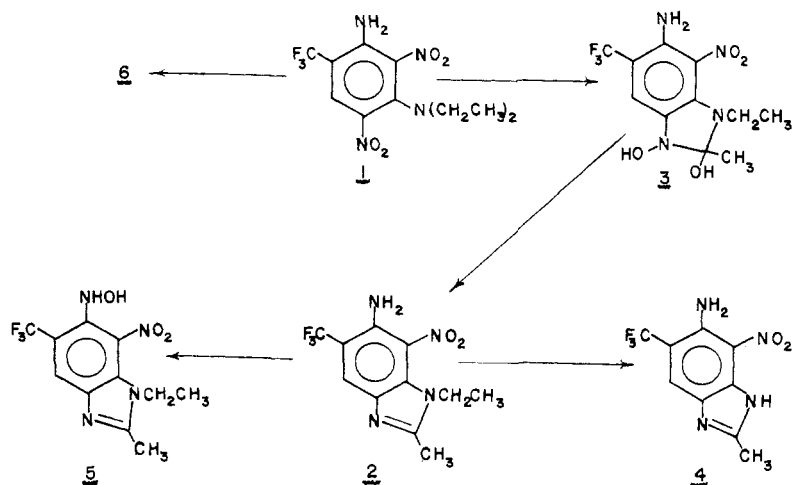
Figure 2. Photolysis products of dinitramine.

mass spectrum showed a parent ion at m/e 304, and the elemental analysis indicated an empirical formula of $C_{11}H_{11}F_3N_4O_3$. Structure 5 is consistent with these data if one assumes that the nmr absorption of the hydroxylamine protons was too broad to be observed.

The mass spectrum of compound 6 suggested a molecular weight of 258 and the elemental analysis was satisfactory for $C_9H_5F_3N_4O_2$. The structure of this product has not been established.

After the above products had been characterized, the effect of sunlight on aqueous dinitramine was examined. A suspension of dinitramine in water (10 ppm in 10 l.) was stirred in the sun for 2 days and then extracted with methylene chloride (a separate experiment with $^{14}CF_3$-labeled dinitramine indicated that about 45% of the degradation products were highly polar materials which remained in the aqueous phase). The organic layer was stripped and the residue fractionated by thin-layer chromatography. Besides unreacted dinitramine, there were three major and three minor products. Two of the major products were identified by superimposable infrared spectra as the previously identified benzimidazole (2) and the benzimidazoline (3). The third major product had an ir spectrum very similar to 2 but was clearly not one of the products identified in the methanol experiments. A mass spectral analysis showed a parent ion of m/e 260. In addition, the fragmentation pattern showed major peaks at 214 ($-NO_2$) and 194 ($-HF$), just as was observed for 2 and 3. It seems likely that this product was the dealkylated benzimidazole (4). Photochemical dealkylation of amines is well documented (Schonberg, 1968).

Figure 2 gives a plausible sequence to account for the observed products. Condensation at the α-carbon leads to benzimidazoline 3, which may lose water and oxygen to provide benzimidazole 2. Formation of 2 from 3 was es-

tablished in a separate experiment in which the benzimidazoline itself was photolyzed in methanol and found to yield benzimidazole 2. Dealkylation and oxidation of 2 could account for 4 and 5, respectively.

The ring-closed compounds obtained from dinitramine suggest the possible formation of similar cyclic photoproducts from other herbicides having a nitro group ortho to an alkylamino group.

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