

The Photolysis of Diphenamid

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Diphenamid (N,N-dimethyl-2,2-diphenylacetamide) is a selective pre-emergence herbicide used in the growing of tomatoes, peanuts, peppers, Irish and sweet potatoes, and strawberries. The metabolism of Diphenamid has been studied in rats (1), tomatoes (2), strawberries (3), and fungal cultures (4). This communication is concerned with another possible degradation pathway for Diphenamid, i. e. photolysis.

Experimental

Irradiation Conditions

Irradiations of 200 ppm Diphenamid in aqueous solution were performed in 1-liter flasks equipped with magnetic stirrer and a Model PCQ 9G-1 6-inch low pressure immersion ultraviolet lamp (available from Ultra-Violet Products, Inc., San Gabriel, California). This lamp emitted 80-90% 2537 Å⁰ light. Solution temperature never exceeded 38⁰. Exposure times varied between 5 hours and 3 days, the products being the same.

Irradiation in sunlight was carried out in a beaker covered by a quartz plate.

Gas Chromatography

A Research Specialties Model 600 Gas Chromatograph was equipped with a flame ionization detector, temperature programmer, T-splitter (5:1), and a 6-foot by 1/4-inch o.d. aluminum column packed with 5% Versamid 900 on HMDS-Treated Chromasorb W, 80-100 mesh. On-column injection was used. Air flow was 240 ml./min. and hydrogen flow (measured with carrier gas flow off at room temperature) was 55 ml./min. Nitrogen carrier gas flow was 120, 97, and 86 ml./min., respectively, at 135°, 188°, and 220°.

Thin Layer Chromatography

Mallinckrodt 0.25 mm.-thick Chroma-Plates 4G were activated for 1 hour at 110°, allowed to cool, and kept dessicated until use. These plates contained approximately 85% silicic acid and 15% calcium sulfate. Spots or streaks were applied about 3 cm. from the edge with 1 ul. pipettes or with a Desaga automatic streaker and developed in the ascending direction. The developed plates were sprayed with a 1% solution of disodium fluorescein and the spots or streaks were visualized with the aid of a short-wavelength ultraviolet lamp.

Isolation and Identification of the Photoproducts

The yellow, irradiated solution was extracted into

ethyl acetate in between treatments with sodium bicarbonate, potassium hydroxide, and hydrochloric acid in order to separate the reaction mixture into acidic, phenolic, basic, and neutral fractions. Less than 1% of the product mixture was found in the phenolic and basic fractions and no further work was done with them.

The acidic fraction consisted mainly of a dark-brown oil which resisted crystallization in a wide variety of solvents, exhibited no g.l.c. peaks on Versamid 900 or SE-30 columns, and exhibited an infrared spectrum characteristic of polymeric material. Sublimation resulted in the isolation of a small amount of material whose infrared spectrum was identical with that of an authentic sample of benzoic acid. No diphenylacetic acid was obtained on continued sublimation.

The components of the neutral fraction were separated by preparative thin-layer chromatography, using benzene-ethyl acetate (70:5) for development. After location of the neutral components on the plate, they were scraped off and eluted from the silica gel with ethyl acetate. Those materials with R_f values lower than 0.3 were found to be mixtures (g.l.c.) and underwent a second preparative thin-layer separation, this time using (70:30) benzene-ethyl acetate. The infrared spectra of the materials thus separated were identical with those of benzophenone, benzhydrol, Diphenamid, and N-methyl-2,2-diphenylacetamide (MDA). Further proof of identity was furnished

by observation of identical t.l.c. R_f values and g.l.c. retention times when compared with authentic samples. Another material ($R_f=0.56$ in 70:30 benzene-ethyl acetate) was obtained in very low yield and exhibited a mass spectrum whose parent ion appeared at m/e 239. This mass spectrum was essentially identical with that of Diphenamid except that it exhibited a fairly large (p-1) peak, indicating the possible presence of an aldehyde group (5). Because demethylation is one of the pathways of Diphenamid photolysis and formamido compounds have been observed as intermediates in the photolytic demethylations of Zectran and Matacil (6), it is suggested that this material is N-formyl-2,2-diphenylacetamide (FDA). Yet another material ($R_f=0.28$ in 70:5 benzene-ethyl acetate) was observed, but no attempt was made at identification.

Results and Discussion

The products of Diphenamid photolysis are tabulated in Table 1 together with their t.l.c. R_f values and g.l.c. retention times. Included in this table is the g.l.c. retention time for 2,2-diphenylacetamide (DA). Although DA is not a photolysis product, it apparently is a metabolite (1-4), and no g.l.c. conditions for the simultaneous determination of Diphenamid, MDA, and DA have previously been published.

The photolytic demethylation of Diphenamid is

TABLE 1

TLC & GLC Characteristics of Diphenamid and its Photoproducts

Compound	TLC R _F Values		GLC Retention Times (minutes)		
	<u>C₆H₆-EtOAc (70:5)</u>	<u>C₆H₆-EtOAc (70:30)</u>	<u>220°</u>	<u>188°</u>	<u>135-220°(a)</u>
Benzophenone	.70	-	-	1.5	4.8
Benzhydrol	.45	-	-	3.3	8.6
Unidentified Material	.28	-	-	7.5	11.5
FDA ???	.22	.56	-	9.5	12.6
Diphenamid	0-.18	.45	4.4	13.2	14.2
MDA	0-.18	.37	8.6	31.1	19.2
DA (b)	-	-	14.2	-	-
Benzoic Acid	.22	.55	-	-	-

(a) Programmed at 10°/min.

(b) DA is not a photoproduct.

consistent with other photolytic reactions involving N-methyl groups. Geissbühler¹¹ and co-workers (7) found that N'-(4-chlorophenoxy)-phenyl-N,N-dimethylurea (Tenoran) was converted to its mono- and di-demethylated derivatives by u.v. light. In addition, the photolytic demethylation of the dimethylaminoaryl moieties in Zectran and Matacil has been demonstrated (6).

Exposure of aqueous solutions of Diphenamid to sunlight resulted in no photodecomposition, even after 30 days. However, the possibility of photosensitization by chloroplast pigments cannot be ignored. Studies along these lines are in progress.

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