

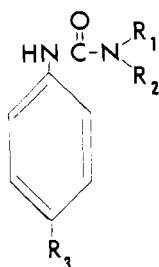
# Photolysis of 3-(*p*-Bromophenyl)-1-methoxy-1-methylurea

Joseph D. Rosen and Richard F. Strusz

As part of a study to determine the environmental fate of pesticides, 3-(*p*-bromophenyl)-1-methoxy-1-methylurea (I), a material representative of a class of economically important herbicides, was exposed to sunlight in aqueous solution. The major product was found to be 3-(*p*-hydroxyphenyl)-1-methoxy-1-methylurea (II). Minor products included 3-(*p*-

bromophenyl)-1-methylurea (III) and *p*-bromophenylurea (IV). Experimental evidence suggested that substituted diphenyl formation had also occurred. Synthetic and chromatographic methods (both gas and thin layer) for the major photoproduct, II, are presented.

The selective, substituted urea herbicide 3-(*p*-bromophenyl)-1-methoxy-1-methylurea (I), commonly known as metobromuron or patoran, is used for weed control in potatoes, corn, safflower, flax, and seeded legumes. The effect of ultraviolet light on several substituted urea herbicides was studied by Hill *et al.* (1955), Weldon and Timmons (1961), and Jordan *et al.* (1963), but no products were identified. Sweester (1963) obtained a monuron-riboflavin adduct by irradiating 3-(*p*-chlorophenyl)-1,1-dimethylurea (monuron) in the presence of riboflavin-5-phosphate. Geissbuhler *et al.* (1963) found that the exposure of solid 3-(*p*-chlorophenoxy)-phenyl-1,1-dimethylurea (tenoran, chloroxuron) to ultraviolet light resulted mostly in carbon dioxide evolution. There was also thin-layer chromatography (TLC) evidence of both mono- and didemethylation as well as unidentified material. Because of the paucity of knowledge concerning the nature of the photolytic products of substituted urea herbicides, especially in water, we have initiated such studies. Metobromuron, because of its relatively high solubility in water (ca. 320 p.p.m.), was chosen as a model compound.



	$R_1$	$R_2$	$R_3$
I	Me	OMe	Br
II	Me	OMe	OH
III	Me	H	Br
IV	H	H	Br
VI	H	OMe	Br

Department of Agricultural Chemistry, Bureau of Conservation and Environmental Science, Rutgers University, New Brunswick, N. J. 08904

## EXPERIMENTAL

**Irradiation Conditions.** Aqueous solutions of I (225 p.p.m.) were covered with Corning C.S. No. 9-54 quartz plates and exposed to sunlight for a 17-day period in late summer. A control solution was covered with taped glass and exposed for the same period. The average daily maximum temperature for the exposure period was 78°F., with a maximum at 85°F. On clear, windless days, the temperatures of the metobromuron solutions were probably 20°F. higher. Under these conditions, the metobromuron in the control solution remained stable.

Photolyses were also carried out by using a low-pressure, 2.5-watt mercury immersion lamp (Model PCQ 9G-1, Ultraviolet Products, San Gabriel, Calif.). Qualitative results (except for one extra product) were similar.

**Isolation of Reaction Products.** The aqueous solution was saturated with sodium chloride and extracted four times with an equal volume of ethyl acetate. The ethyl acetate layers were combined, dried over anhydrous sodium sulfate, filtered, and concentrated for quantitation by gas-liquid chromatography (GLC) and for separation by preparative TLC.

**Thin-Layer Chromatography.** The ethyl acetate extract (50 mg. per ml.) of the sunlight-irradiated solutions was separated on silica gel G plates (500-micron) using two solvent systems developed by Katz and Fassbender (1968). The first solvent system (A), which consisted of chloroform-pyridine-methanol (100:10:1), separated the mixture into three streaks which could be visualized by two spray reagents: silver nitrate solution followed by exposure to ultraviolet light (Mitchell, 1961) and ferric chloride-potassium ferricyanide solution (Bobbitt, 1963). Under these conditions, I had  $R_f = 0.86$ , II = 0.67, and an unidentified material (V) had  $R_f = 0.80$ . The latter material

was separated from I by use of a second solvent system (B), consisting of chloroform-acetic acid (60 to 1), in which I had  $R_f = 0.54$  and V had  $R_f = 0.34$ . The materials so obtained were then subjected to mass and/or infrared spectroscopy (KBr micropellet).

The ethyl acetate extract of the ultraviolet-irradiated solution gave, in addition to the materials above, materials with  $R_f$  values at 0.57, 0.24, and 0.17 in solvent system A. Elution of the latter two materials gave infrared spectra identical to those of authentic III and IV, respectively.

Qualitative TLC on Eastman sheets (100-micron) using solvent systems A and C (ethyl acetate) suggested that III and IV were also present in the sunlight-irradiated solution but that the material with  $R_f = 0.57$  was not. Chromatography in solvent system B also indicated that this material was not 3-(*p*-bromophenyl)-1-methoxyurea (VI).

**Gas-Liquid Chromatography.** Quantitative determination of the major reaction product and qualitative determination of minor products were performed on a Microteck MT-220 gas chromatograph equipped with a flame ionization detector and a  $\frac{1}{4}$ -inch O.D., 16-inch glass column containing 1.5% XE-60 on Gas Chrom Q, 80- to 100-mesh. Carrier gas velocity was 80 ml. per minute. By programming at 5° per minute between 130° and 210° C., the following retention times were obtained; I, 6.5; II, 11.25; III, 13.5; IV, 14.5; V, 6, 10, and 11.25 minutes. The observation of a shoulder near 11.25 when II and V were cochromatographed indicated that II was not a contaminant of V. The contribution of V to the area of the peak at 11.25 minutes when the entire mixture was chromatographed was negligible because of the observed absence of the 6- and 10-minute peaks at the sensitivities used for quantitation. The GLC conditions were adapted from those developed by Katz and Strusz (1968) for the separation of the metabolites of a number of substituted urea herbicides.

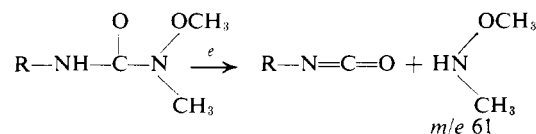
**Synthesis of II.** Five-hundred milligrams (0.326 mmole) of *p*-hydroxybenzazide, prepared by the method of Curtius *et al.* (1895), and 70 ml. of dry toluene were heated at 90°C. for 2 hours. Gas evolution was observed as the material went into solution. An aliquot of the reaction solution was evaporated under reduced pressure; the infrared spectrum showed the loss of acyl azide absorption at 2127 and 2173  $\text{cm}^{-1}$  and the presence of isocyanate absorption at 2257  $\text{cm}^{-1}$ . The solution was then treated with *O,N*-dimethylhydroxylamine (Aldrich Chemical Co.) and allowed to stand for 1 hour with occasional shaking. After evaporation of the solvent under reduced pressure, the residue, upon recrystallization from ethanol, gave white crystals (m.p. 142–44°). The infrared spectrum of the material was similar to that of I, exhibiting, in addition, phenol absorption at 3162 and 1208  $\text{cm}^{-1}$ . There was no isocyanate absorption. Elemental analysis: Calculated for  $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_3$ , C 55.10, H 6.12; found C 54.82, H 6.37.

## RESULTS AND DISCUSSION

A 17-day exposure of I to sunlight in aqueous solution resulted in a mixture containing 80% unchanged metobromuron and 15% 3-(*p*-hydroxyphenyl)-1-methoxy-1-

methylurea (II). The remaining material consisted of at least three compounds: 3-(*p*-bromophenyl)-1-methylurea (III), *p*-bromophenylurea (IV), and the unidentified material or materials (V). In addition, there was probably some hydrobromic acid, as suggested by a pH drop to 4.1. The sensitivity of the gas chromatograph had to be increased 400 times to see the peaks of III, IV, and V. No evidence of the presence of 3-(*p*-bromophenyl)-1-methoxyurea, retention time = 9.25 minutes, was obtained even at this increased sensitivity. It is inferred, therefore, that demethoxylation occurred in preference to demethylation. Although no spectroscopic or chemical confirmation for the formation of III and IV in sunlight was obtained, the evidence of their presence in the reaction mixture (TLC, GLC, and infrared spectra of materials isolated from laboratory-irradiated solutions) is fairly conclusive. Similar photolytic reactions have been observed for tenoran (Geissbuhler *et al.*, 1963), zectran and matacil (Abdel-Wahab and Cassida, 1967), and diphenamid (Rosen, 1967).

The unidentified material or materials, V, exhibited a mass spectrum whose highest mass occurred at  $m/e$  438. Peaks at  $m/e$  377 and  $m/e$  316 (loss of two mass 61 fragments) indicated the presence of two substituted urea groups (Benson and Damico, 1968). Isotope distributions indicated the presence of only one bromine atom (Beynon,



1960). Such a spectrum suggests dimerization of I accompanied by loss of hydrobromic acid. However, the material exhibited two positive phenol tests (ferric chloride-potassium ferricyanide solution; 0.5% 4-aminoantipyrine in pH 8 buffer followed by a 2% aqueous solution of potassium ferricyanide) and its gas chromatogram consisted of at least three peaks. Because of the small amount of material obtained, we could not determine whether V was pure or consisted of a mixture of products and we have not been able to characterize it further. It is apparent, however, that a minor pathway of metobromuron photolysis involves "dimerization." Recently, Joschek and Miller (1966) found that 4,4-dihydroxybiphenyl was one of the products of the photolysis of 4-bromophenol in water. The analogous compound in our system should have exhibited a parent ion at  $m/e$  358, but such a peak was not found.

The major reaction product was the phenol, II. Its mass spectrum exhibited a parent ion at  $m/e$  196 and a base peak at  $m/e$  135 (loss of 61). Isotope distribution indicated loss of bromine. Confirmation of the structure of II was obtained by comparison of the infrared spectra, TLC  $R_f$  values (in three solvent systems), and GLC retention times of the isolated material with those of material obtained by synthetic methods. The photolytic conversion of halogenated aromatics to phenols is a relatively new reaction,

having only recently been observed in the conversion of bromophenols to dihydroxybenzenes (Joschek and Miller, 1966), the degradation of 2,4-dichlorophenoxyacetic acid (Crosby and Tutass, 1966), and the transformation of *o*-chlorobenzoic acid to salicylic acid (Crosby, 1966). The toxicology, persistence, and metabolism of II are unknown. Such studies are planned.

#### ACKNOWLEDGMENT

The authors are indebted to Joseph N. Damico and Fred Ives, Food and Drug Administration, for the mass spectrum of II, and to V. F. Boyd, CIBA Agrochemical Co., for the supply of model compounds.

The mass spectrum of V was determined by Gollab Analytical Service, Berkeley Heights, N. J., and the elemental analysis by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

#### LITERATURE CITED

- Abdel-Wahab, A. M., Cassida, J. E., *J. Agr. Food Chem.* **15**, 479 (1967).  
Benson, W. R., Damico, J. N., *J. Assoc. Offic. Anal. Chemists* **51**, 347 (1968).  
Beynon, J. H., "Mass Spectrometry and Its Applications to Organic Chemistry," p. 298, Elsevier, Amsterdam, 1960.  
Bobbitt, J. M., "Thin Layer Chromatography," p. 94, Reinhold, New York, 1963.  
Crosby, D. G., Division of Agricultural and Food Chemistry, 152nd Meeting, ACS, New York, N. Y., September 1966.  
Crosby, D. G., Tutass, H. O., *J. Agr. Food Chem.* **14**, 596 (1966).  
Curtius, T., Strauve, A., Radenhausen, R., *J. Prakt. Chem.* **52** (2), 227 (1895).  
Geissbuhler, H., Haselbach, C., Aebi, H., Ebner, L., *Weed Res.* **3**, 277 (1963).  
Hill, G. D., McGahen, J. W., Baker, H. M., Finnerty, D. W., Bingeman, C. W., *Agron. J.* **47**, 93 (1955).  
Jordan, L. S., Coggins, C. W., Day, B. E., Clerx, W. A., *Weeds* **12**, 1 (1963).  
Joschek, H. I., Miller, S. I., *J. Am. Chem. Soc.* **88**, 3269 (1966).  
Katz, S. E., Fassbender, C. A., *Weeds*, in press (July 1968).  
Katz, S. E., Strusz, R. F., Rutgers University, New Brunswick, N. J., unpublished information, 1968.  
Mitchell, L. C., *J. Assoc. Offic. Anal. Chemists* **44**, 643 (1961).  
Rosen, J. D., *Bull. Environ. Contam. Toxicol.* **2**, 349 (1967).  
Sweester, P. B., *Biochim. Biophys. Acta* **66**, 78 (1963).  
Weldon, L. W., Timmons, F. L., *Weeds* **9**, 111 (1961).

Received for review February 27, 1968. Accepted April 18, 1968.  
Paper of the Journal Series, New Jersey Agricultural Experiment Station, Rutgers—The State University, New Brunswick, N. J.  
This research was supported by U.S.P.H.S. Research Grant ES-00016 from Bureau of State Services.